Biodegradation Of Alternative Fuel Oxygenates And NDMA In The Environment

USGS Research

Toxic Substances Hydrology Program:

toxics.usgs.gov

Fuel Oxygenates:

toxics.usgs.gov/investigations/petroleum_contamination.html

Emerging Water Quality Issues:

toxics.usgs.gov/regional/emc/index.html

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Presentation Outline

- Relative Biodegradation of MTBE, TBA, and TAME in Surface-Water Sediments.
- Effect of Redox Condition on TBA Biodegradation in Surface-Water Sediments.
- Biodegradation of NDMA in Soil at a Water Reclamation Facility.

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Relative Biodegradation of MTBE, TBA, and TAME in Surface-Water Sediments

Relative Biodegradation of MTBE, TBA, and TAME in Surface-Water Sediments

- Long Island, New York:
  - Five surface-water systems (bays, streams, and pond)
  - Fresh-water to salt-water systems.
  - Characterized by discharge of gasoline-contaminated, groundwater.
- Microcosm study:
  - Oxic and anoxic.
  - 14C-substrates:
    - [methyl-^{14}C] TAME
    - [U-^{14}C] MTBE
    - [U-^{14}C] TBA
  - Mineralization – degradation to innocuous products ($^{14}CO_2$ & $^{14}CH_4$).
  - 83 days incubation.

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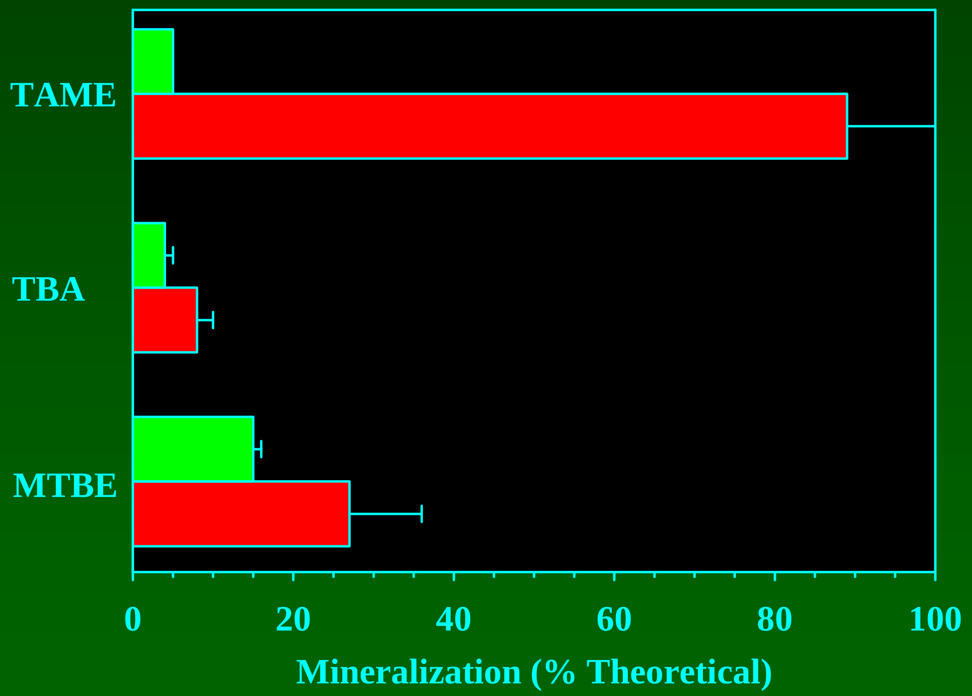
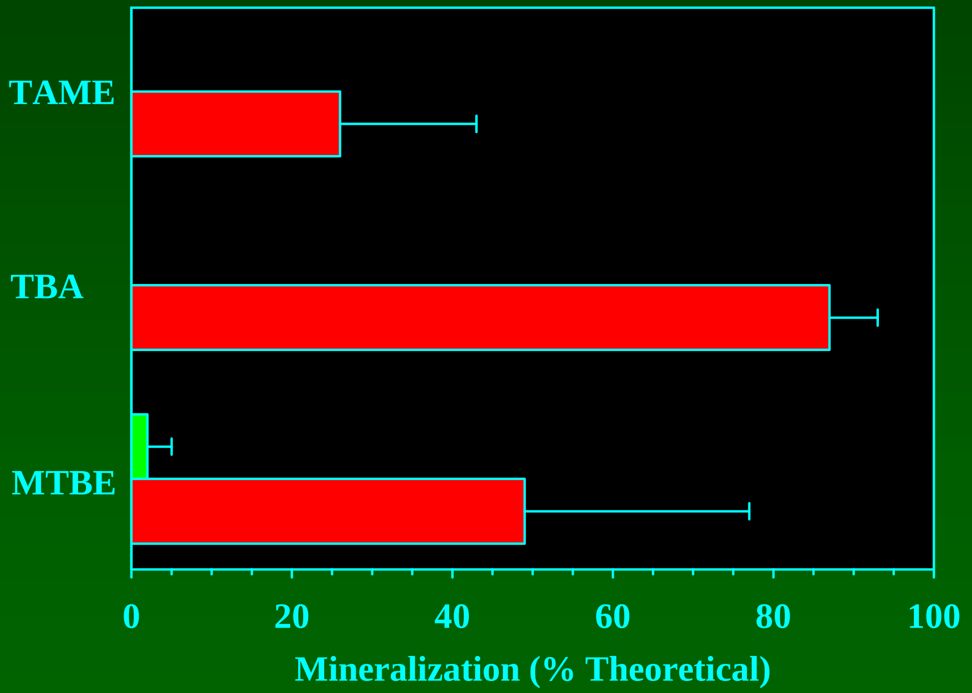
Fort Pond



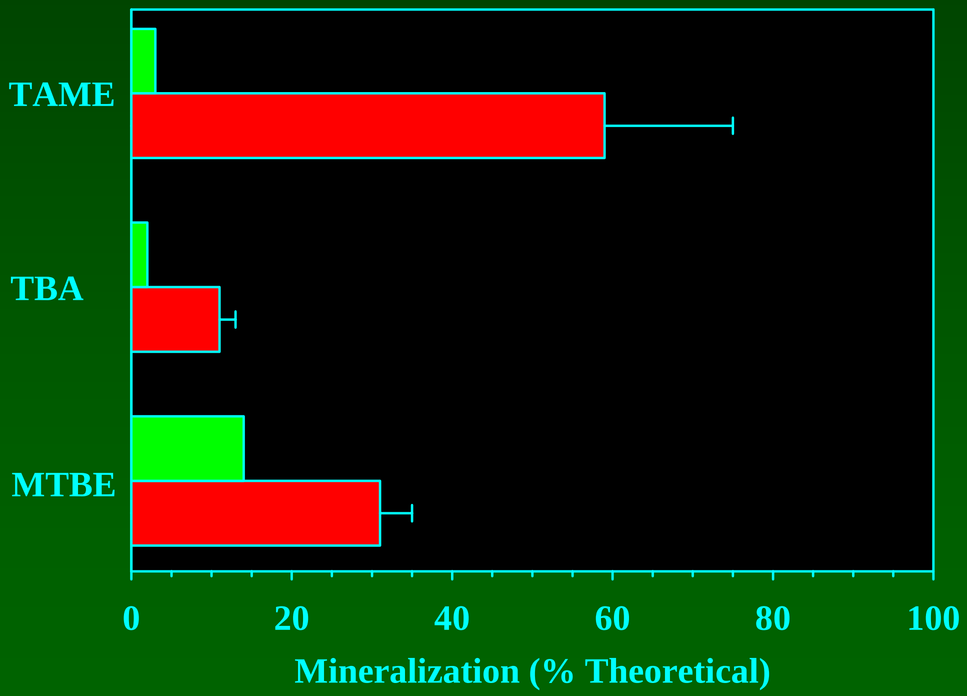
- Fresh-water pond.
- Oxygenate mineralization:
  - TAME – most.
  - TBA - least.
- Redox effect:
  - Oxic:
    - More efficient.
    - $^{14}CO_2$
  - Anoxic:
    - Methanogenic.
    - Less efficient.
    - $^{14}CO_2$ and $^{14}CH_4$

Great South Bay - Beach



- Salt-water bay.
- Oxygenate mineralization:
  - TBA – most.
  - TAME - least.
- Redox effect:
  - Oxic:
    - More efficient.
    - $^{14}CO_2$
  - Anoxic:
    - SO_4-reducing.
    - Insignificant to poor.
    - $^{14}CH_4$

Great South Bay – Tidal Creek



- Brackish creek.
- Oxygenate mineralization:
  - TAME – most.
  - TBA - least.
- Redox effect:
  - Oxic:
    - More efficient.
    - $^{14}CO_2$
  - Anoxic:
    - SO_4-reducing, methanogenic.
    - Less efficient.
    - $^{14}CO_2$ and $^{14}CH_4$

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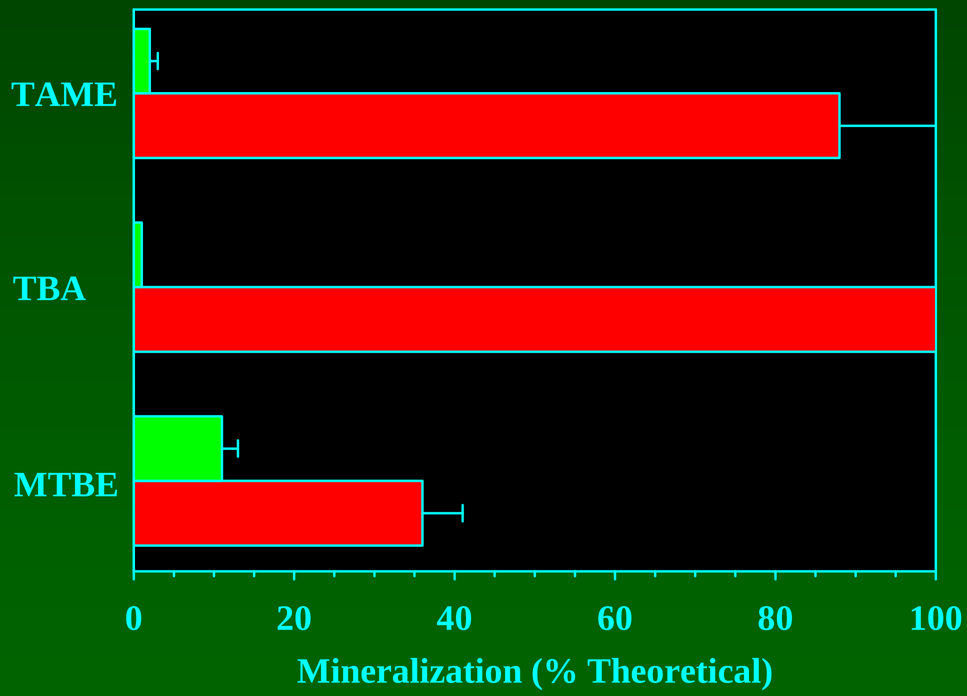
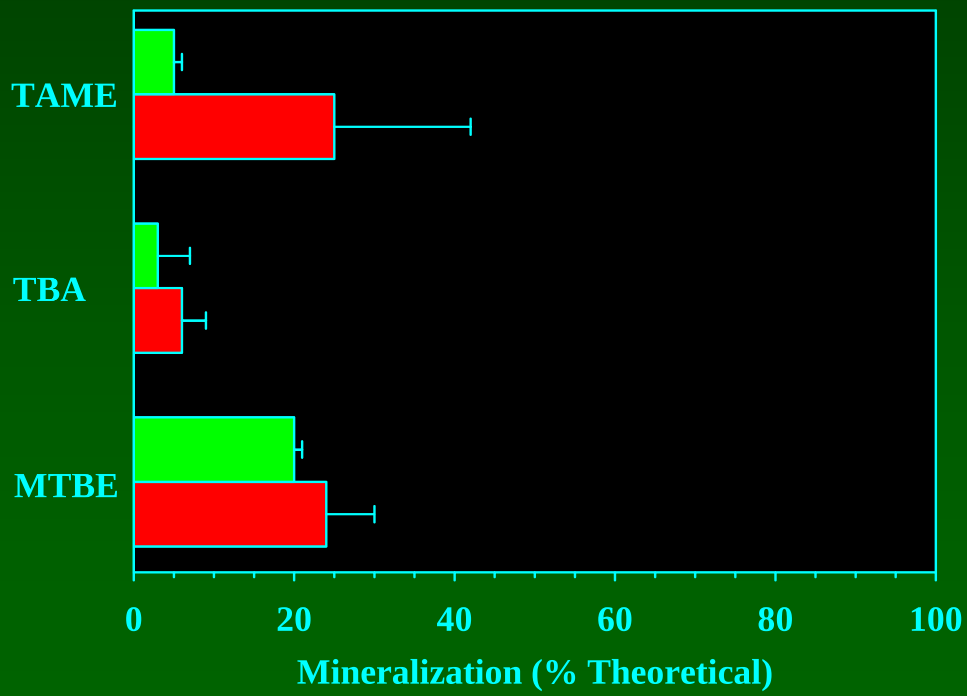
Carmans River



- High DOC, fresh-water river.
- Oxygenate mineralization:
  - TAME & TBA – most.
  - MTBE - least.
- Redox effect:
  - Oxic:
    - More efficient.
    - $^{14}CO_2$
  - Anoxic:
    - Methanogenic.
    - Less efficient.
    - $^{14}CO_2$ and $^{14}CH_4$

Tiana Bay



- Brackish bay.
- Oxygenate mineralization:
  - TAME & MTBE – most.
  - TBA - least.
- Redox effect:
  - Oxic:
    - Somewhat more efficient.
    - $^{14}CO_2$
  - Anoxic:
    - Methanogenic.
    - Less efficient.
    - $^{14}CO_2$ and $^{14}CH_4$

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Relative Biodegradation of Oxygenates: Conclusions

- Mineralization of all three fuel oxygenate compounds was apparent in each system under oxic conditions.
  - 10-100% mineralization to $^{14}CO_2$.
  - Relative biodegradability varied widely from system to system.

- Mineralization of all fuel oxygenates was depressed under anoxic conditions.
  - Anoxic biodegradation of TAME and TBA ranged from poor to insignificant.
  - In general, anoxic mineralization of MTBE ranged from 40 to 95% of oxic MTBE mineralization.

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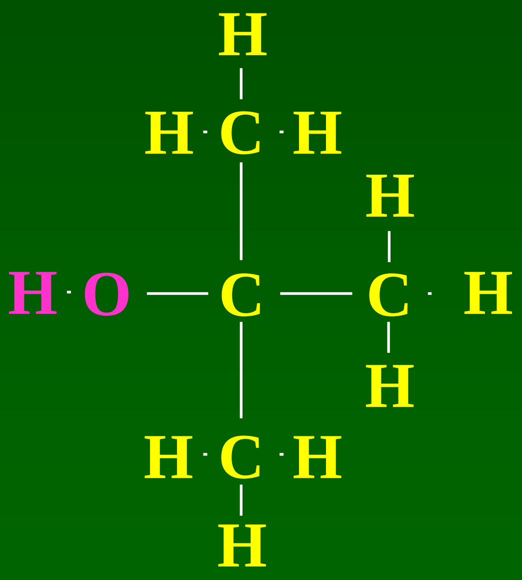
Effect of Redox Condition on TBA Biodegradation in Surface-Water Sediments

t-Butyl Alcohol (TBA)

Formula: $C_4H_{10}O$

Structure:



t-Butyl Alcohol (TBA)

- Fuel oxygenate.
- MTBE transformation product/degradation intermediate.
  - Reducing conditions.
- Miscible in water (316g/L @ 25C).
- Animal carcinogen (Cirvello et al 1995).

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Environ. Sci. Technol. **1999,** *33,* 1877–1879

Aerobic Mineralization of MTBE and *tert*-Butyl Alcohol by Stream-Bed Sediment Microorganisms

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Microorganisms indigenous to the stream-bed sediments at two gasoline-contaminated groundwater sites demonstrated significant mineralization of the fuel oxygenates, methyl *tert*-butyl ether (MTBE) and *tert*-butyl alcohol

μg/L; *3, 10, 11*). In contrast, leakage from underground gasoline storage tanks and subsequent discharge of contaminated groundwater can deliver high concentrations of fuel oxygenates to local surface water systems (*3, 4, 13,* this study). At a gasoline spill site in Beaufort, SC, for example, contaminated groundwater containing 10 000 μg/L dissolved MTBE is presently discharging to a nearby stream (*4*). However, groundwater discharging to a surface water body must pass through bed sediment microbial communities that are often highly active, metabolically diverse, and capable of efficient degradation of otherwise recalcitrant compounds (*14–17*). Thus, the potential exists that bed-sediment microbial communities can degrade MTBE and TBA and significantly diminish the impact of these contaminants on surface water quality. The purpose of this paper is to present evidence that bed sediment microorganisms can rapidly degrade MTBE and TBA to nontoxic products. These microbial processes, in turn, may constitute a significant

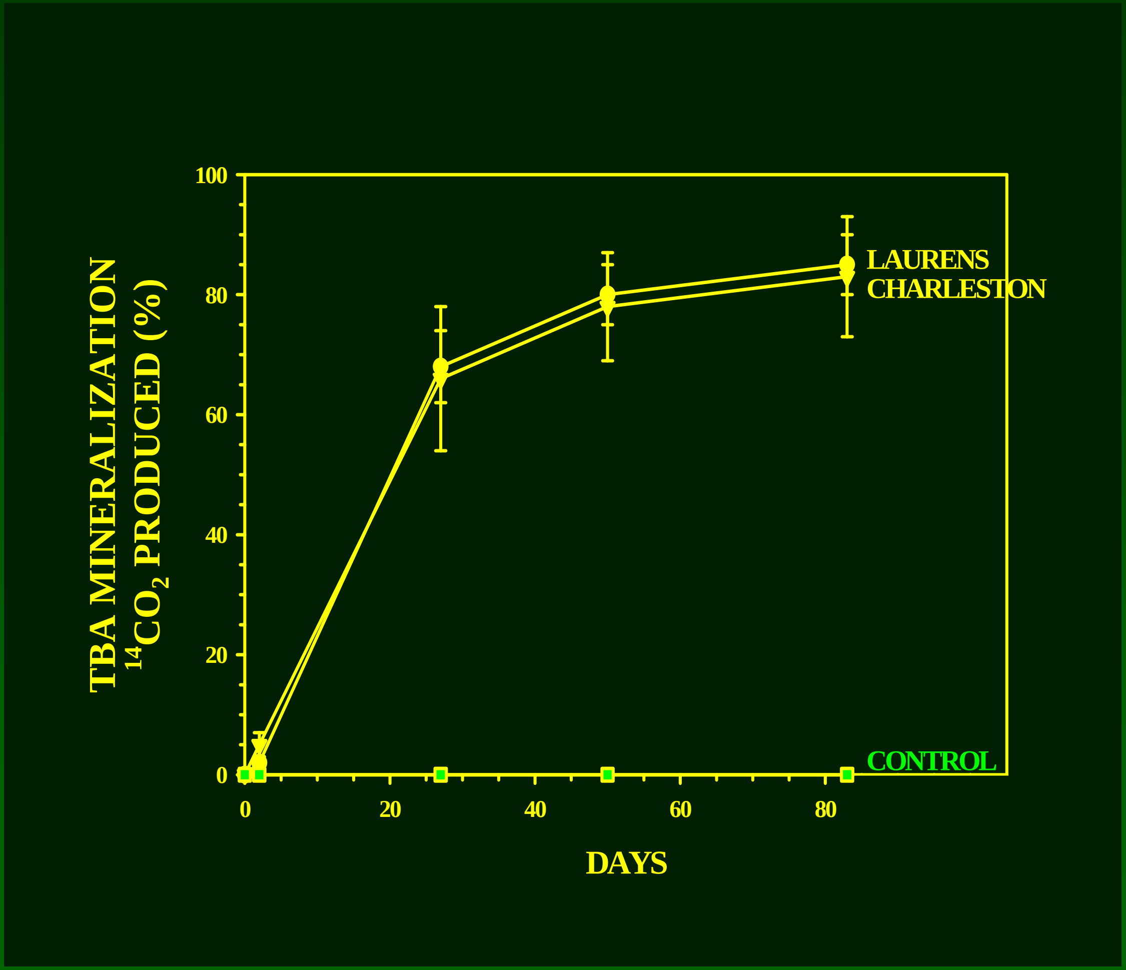
Laurens

- Former gasoline station
- Max [MTBE] = 64 mg/L
- Max [TBA] = 14 mg/L
- Bed sediments
  - Coarse sand
  - 0.8 % organic content

Charleston

- Former gasoline station
- Max [MTBE] = 138 µg/L
- Max [TBA] = 2094 µg/L
- Bed sediments
  - Organic rich silt/clay
  - 17 % organic content

Oxic TBA Biodegradation



- >80% in 80 d.
- Biotic process.
- No accumulation of intermediates.
- $^{14}CO_2$.

Anoxic TBA Biodegradation?

- Methanogenic microcosms.
- No significant degradation observed.
- No significant mineralization observed.

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TBA Biodegradation in Surface-Water Sediments under Aerobic and Anaerobic Conditions

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The potential for [U-^{14}C] TBA biodegradation was examined in laboratory microcosms under a range of terminal electron accepting conditions. TBA mineralization to CO_2 was substantial in surface-water sediments under oxic, denitrifying, or Mn(IV)-reducing conditions and

Methods

Chemicals. TBA mineralization was investigated using uniformly labeled [U-^{14}C] TBA (Moravek Biochemicals, Brea, CA) as described previously (*14*). The radiochemical composition of the [U-^{14}C] TBA stock (5 mCi/mmol specific activity) was evaluated in our lab by direct injection radiometric detection high performance liquid chromatography (HPLC/RD) and direct injection radiometric detection gas chromatography (GC/RD) and found to be greater than 99% ^{14}C-TBA. $H^{14}CO_3^-$ (Sigma Biochemicals, St. Louis, MO) and $^{14}CH_4$ (New England Nuclear, Boston, MA) were used as radiolabeled standards for calibration and methods development. Both had radiochemical purities > 98%.

Study Sites. The ability of surface-water microorganisms to degrade TBA was examined in surface-water sediments from Laurens, SC and Charleston, SC. The dynamic metabolic character of the microbial communities in shallow stream systems makes stream-bed sediments a useful hydrologic system for examining the effect of various redox conditions on the potential for microbial degradation of TBA in the

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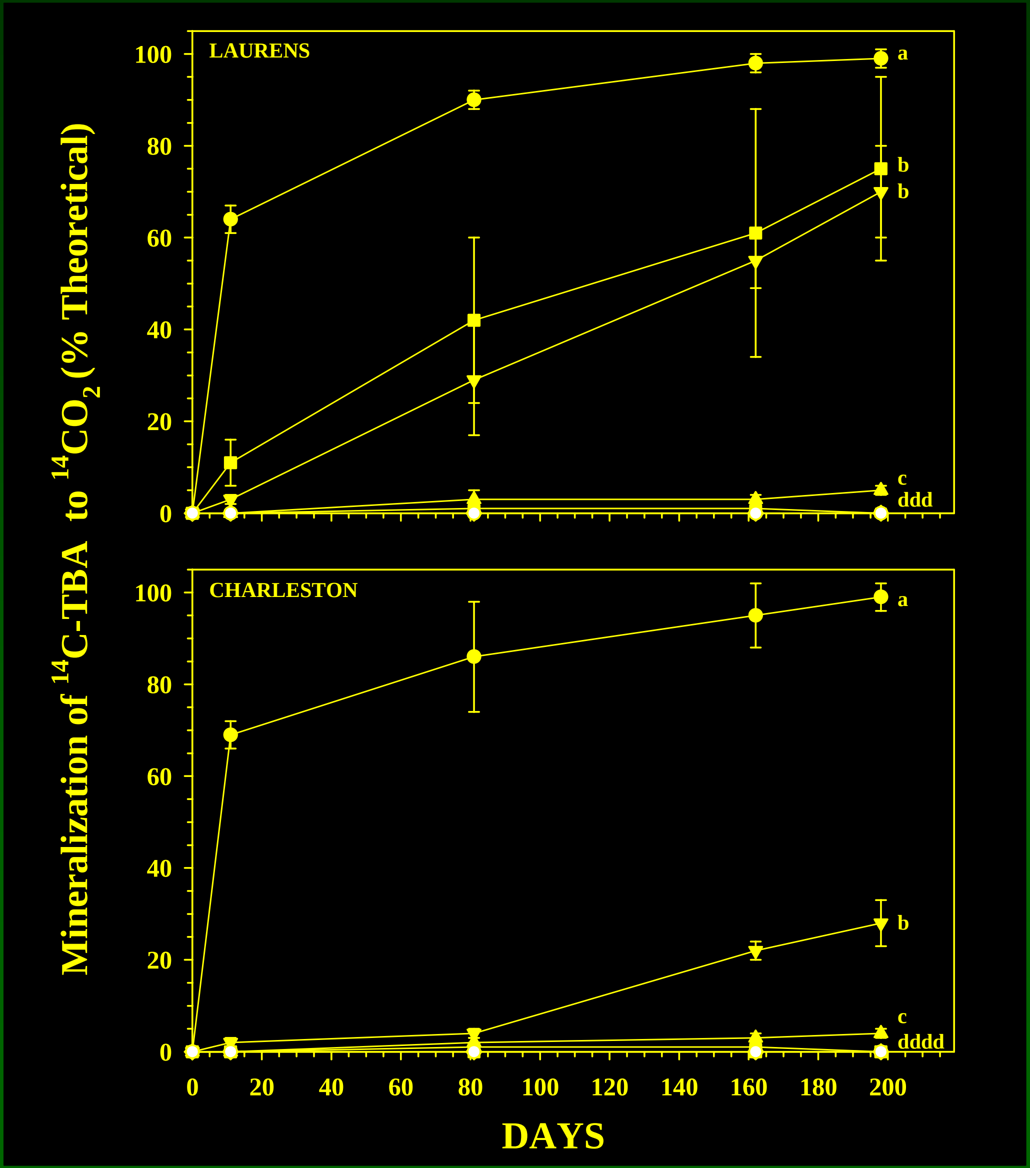
TBA Biodegradation and Redox



- Oxic degradation:
  - Efficient.
  - No intermediates.
- Anoxic:
  - NO_3 reducing (efficient).
  - Mn reducing (efficient).
  - SO_4 reducing (low).
- No degradation of TBA under methanogenic conditions or in sterile control microcosms.

TBA Biodegradation in Surface-Water Sediments

- Efficient biodegradation under oxic conditions.
- Significant potential for biodegradation under Mn(IV)-reducing, NO_3-reducing, and SO_4-reducing conditions.
- No degradation under methanogenic conditions.
- No degradation under heat-sterilized conditions.

Biodegradation of NDMA in Soil at a Water Reclamation Facility

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Biodegradation of *N*-nitrosodimethylamine in Soil from a Water Reclamation Facility

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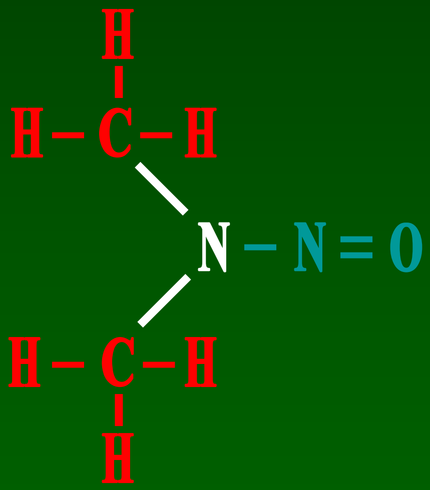
ABSTRACT The potential introduction of *N*-nitrosodimethylamine (NDMA) into groundwater during water reclamation activities poses a significant risk to groundwater drinking supplies. Greater than 54% biodegradation of *N*-[methyl-^{14}C]NDMA to $^{14}CO_2$ or to $^{14}CO_2$ and $^{14}CH_4$ was observed in soil from a water reclamation facility under oxic or anoxic conditions, respectively. Likewise, biodegradation was significant in microcosms containing soil with no history of NDMA contamination. These results indicate that aerobic and anaerobic biodegradation of NDMA may be an effective component of NDMA attenuation in water reclamation facility soils.

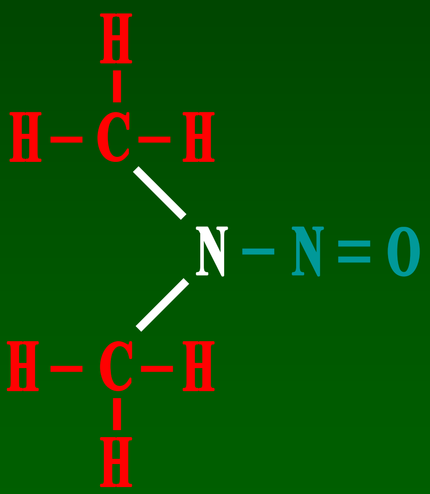
KEYWORDS biodegradation, ground water, NDMA, *N*-nitrosodimethylamine, recharge, soil, water reclamation

Biodegradation of NDMA in Soil at a Water Reclamation Facility



N-Nitrosodimethylamine

Biodegradation of NDMA in Soil at a Water Reclamation Facility



- Multiple anthropogenic sources:
  - Rocket fuel byproduct.
  - Nitroaromatic explosives byproduct.
  - Water treatment byproduct.
- Toxin – Poison.
- Animal Carcinogen.
- Anticipated Human Carcinogen.
- Miscible in water.
- Drinking Water Standard – 10 ng/L (California Department of Health Services).

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NDMA In Reclaimed Water: Threat to Drinking Water Supplies

- [*NDMA*] up to 100 ng/L in treated water.
- Water reclamation involves passive infiltration at spreading grounds or direct injection.
- Two drinking water supply wells in California removed from service in 2000 due to 30-40 ng/L NDMA.
- NDMA attributed to aquifer (phreatic zone injection) recharge activities at reclamation facility.

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Rio Hondo Spreading Grounds

- Montebello Forebay Groundwater Recharge Project in Los Angeles County, California
- RHSG soil microorganisms capable of NDMA biodegradation?
  - Conditions?
  - Efficiency?
  - Mechanisms?
  - Who?

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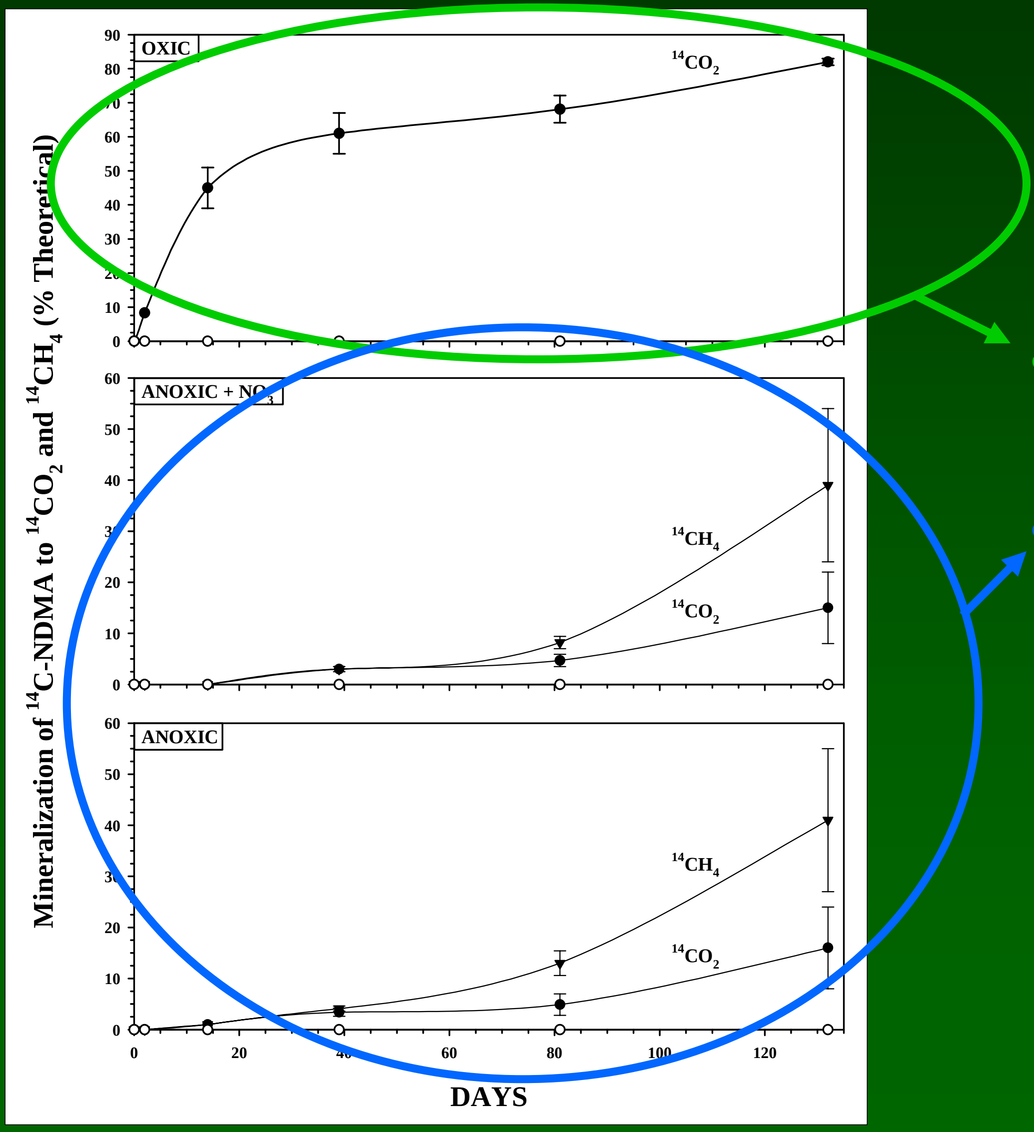
NDMA Biodegradation at RHSG



- Rapid oxic mineralization to $^{14}CO_2$.
- Significant but less efficient mineralization to $^{14}CO_2$ and $^{14}CH_4$ under anoxia.
  - Dissimilatory NO_3 reducing.
  - Methanogenic.

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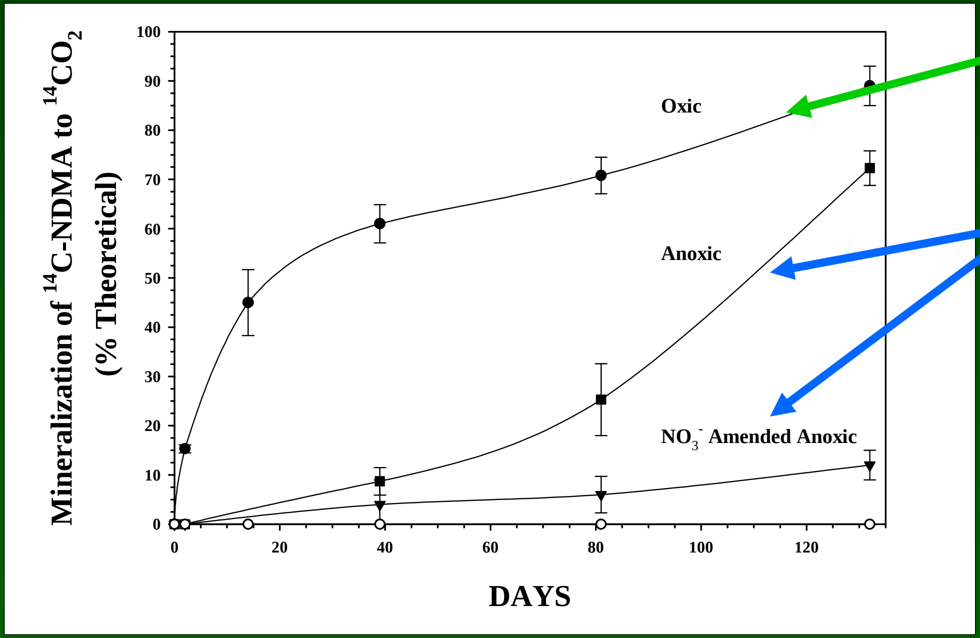
NDMA Biodegradation in Background Soil



- Rapid oxic mineralization to $^{14}CO_2$.
- Significant but less efficient mineralization to $^{14}CO_2$ and $^{14}CH_4$ under anoxia.
  - Mixed anoxic conditions.
  - Dissimilatory NO_3 reducing.

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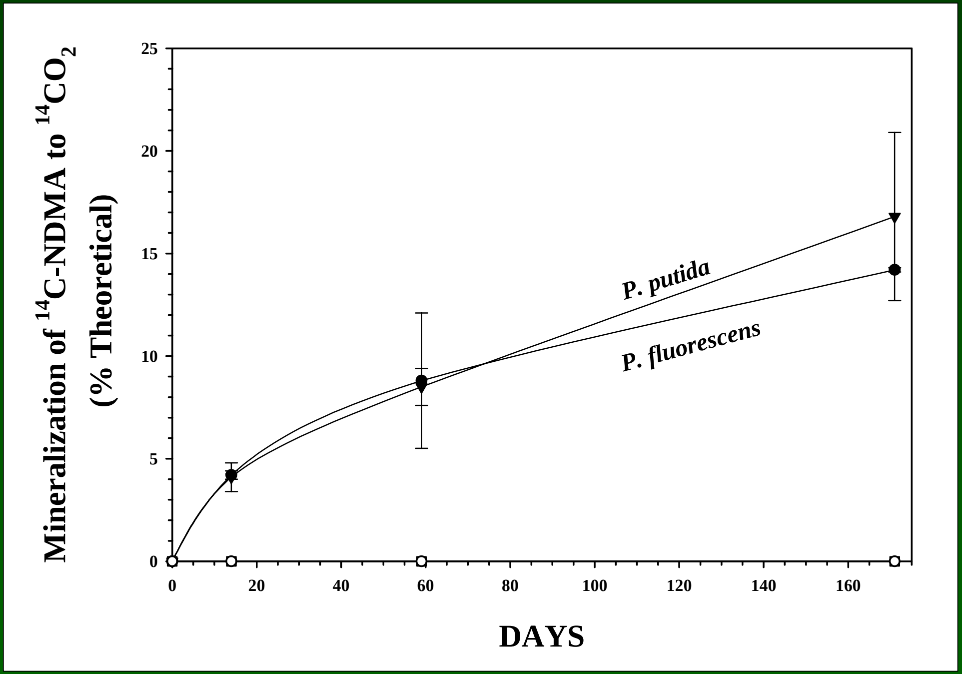
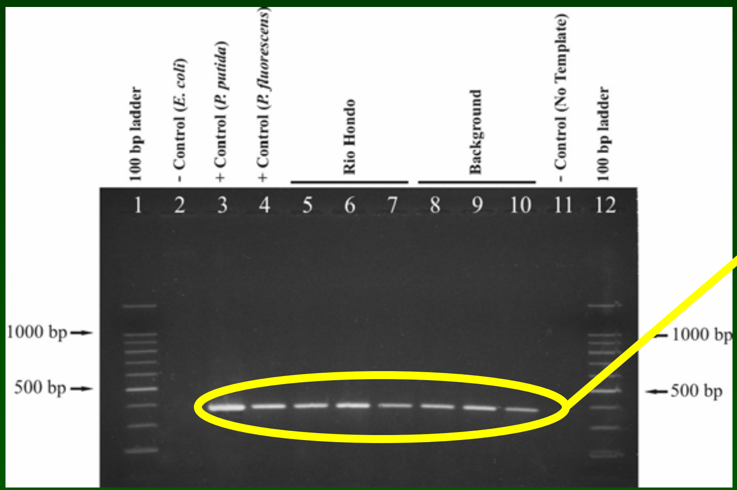
Responsible Microorganisms?

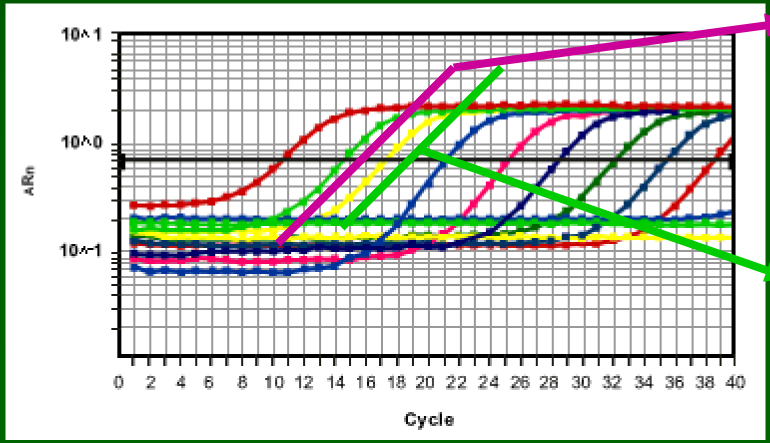


- *Pseudomonas sp.* capable of NDMA degradation to $^{14}CO_2$ under oxic conditions in laboratory.
- *Pseudomonas sp.* Expected to be common in treatment facility soils and background soils.
- PCR to verify.

Pseudomonas-Specific Q-PCR



- *Pseudomonas sp.* present in RHSG and background soils



RHSG – 4.2 X 10^6 Pseudomonas cells/ g soil

BKG – 1.8 X 10^5 Pseudomonas cells/ g soil

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NDMA Conclusions

- Significant potential for NDMA biodegradation in acclimated and non-acclimated soil.

- Significant potential for NDMA biodegradation under oxic and anoxic conditions.

- **Significant potential for NDMA biodegradation in environment under oxic and anoxic conditions.**

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