Field Treatment of MTBE Contaminated Groundwater Using AOP

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Introduction

- Study was conducted by Shaw Environmental, Inc. (Shaw) under subcontract by New Mexico State University (NMSU)
- This evaluation was performed for the U.S. Environmental Protection Agency's (EPA's) Water Supply and Water Resources Division (WSWRD) under EPA Contract No. EP-C-04-034

Disclaimer

- Any opinions expressed in this article are those of the author(s) and do not, necessarily, reflect the official positions and policies of the U.S. Environmental Protection Agency (EPA).
- Any mention of products or trade names does not constitute recommendation for use by EPA.

MTBE BACKGROUND

- EPA has classified Methyl-tertiary butyl ether (MTBE) as a Group C chemical, or as a possible human carcinogen.
- EPA's advisory board recommends a limit of 20 to 40 micrograms per liter (µg/L) for drinking water as the range that is low enough to prevent human health risk.

MTBE Environmental Sources

- Primary Source are LUSTs
- Secondary sources:
  - Vehicle exhaust emissions
  - Spillage and evaporation during the manufacture and transport of MTBE and gasoline containing MTBE
  - Accidental spills or exhaust from boats and personal water craft

Conventional Treatment Technologies

- Air stripping and adsorption transfer the contaminants from one phase into another
- Biological treatment and conventional chemical oxidation have low removal rates

FUNDAMENTALS OF AOP

- MTBE can be oxidized through various AOPs such as:
  - Ozone/hydrogen peroxide
  - Hydrogen peroxide/ultraviolet light (UV)
  - Titanium dioxide (TiO_2) photocatalysis
  - UV/O_3 (this study)

Chemistry of UV/O_3 AOP

- Photolysis of O_3

$$O_3 + H_2O \xrightarrow{h\upsilon} H_2O_2 + O_2$$

- Formation of OHº radicals

$$2O_3 + H_2O_2 \rightarrow 2OH^{\circ} + 3O_2$$

- Hydrogen abstraction (formation of organic compound radical, Rº with H loss)

$$OH^{\bullet} + RH \longrightarrow H_2O + R^{\bullet}$$

Organic Breakdown in AOP

- The organic radical can further initiate several reactions to form other intermediate organic compounds.
- The intermediates may also be toxic, and therefore, must be considered during the design process.
- Given sufficient time for reaction, OH^{o} is capable of completely mineralizing the parent compound.

Breakdown Products

Compound	*Abbrev.*	*Formula*
Methyl-tert butylether	MTBE	$CH_3OC(CH_3)_3$
t-butyl formate	TBF	$C_5H_{10}O_2$
t-butyl alcohol	TBA	$(CH_3)_3COH$
Isopropyl alcohol	IPA	$(CH_3)_2CHOH$
Acetone	Ac	$(CH_3)_2CO$
Methyl acetate	MAc	CH_3COOCH_3
Carbon Dioxide	CO_2	CO_2

Goals

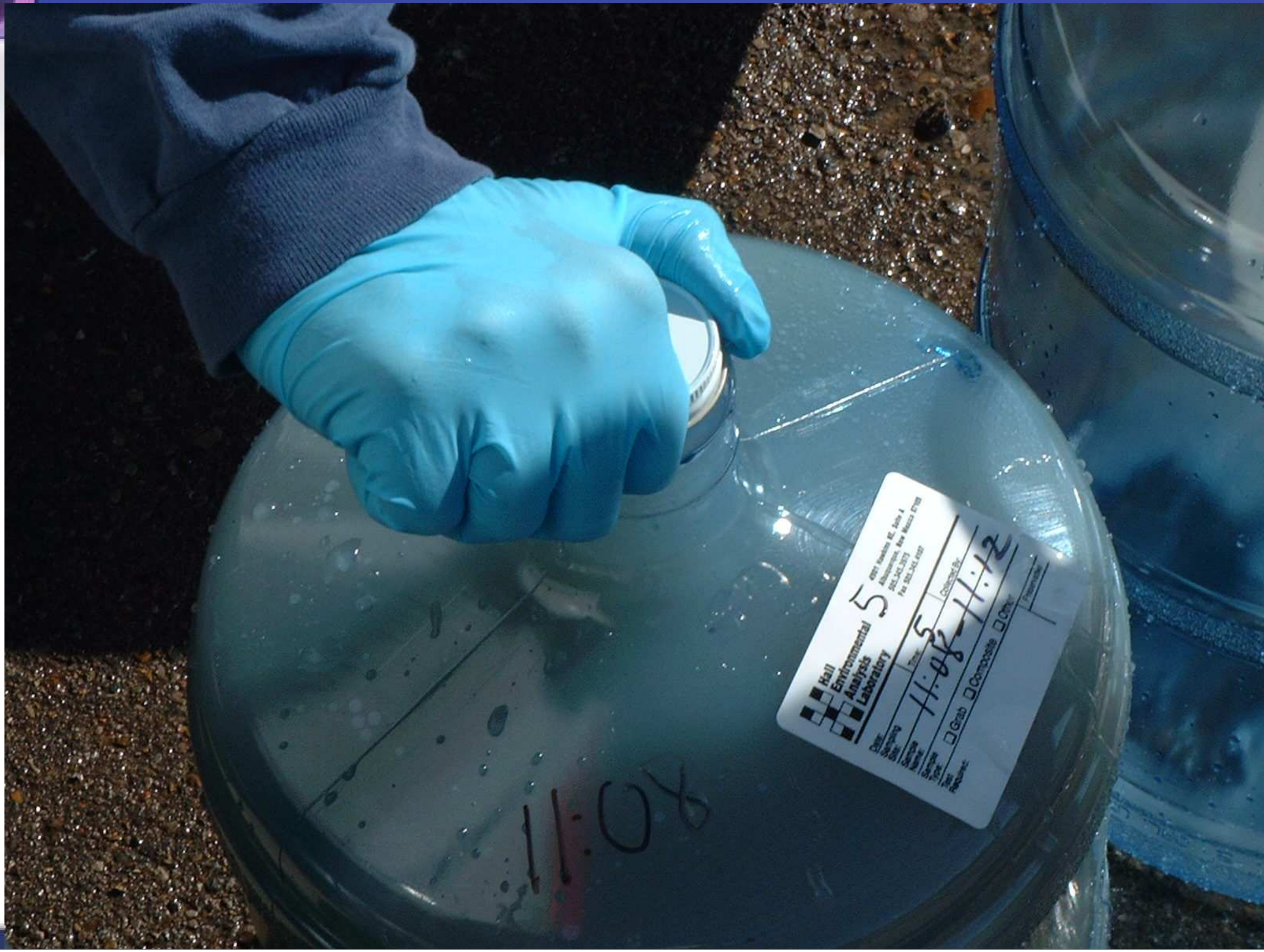
- Test effectiveness of AOP (O_3/UV) in field conditions:
  - Technical
  - Economics
- In low concentration range (difficult to remove) of 30 – 300 ppb MTBE

Site Selection

- High MTBE:BTEX 30,000:3,000 difficult to find)
- Brewer Station 1 in Roswell, NM
- Samples transported to NMSU in Las Cruces
- Dilute samples to 30 – 300 ppb range (hardest range to treat)

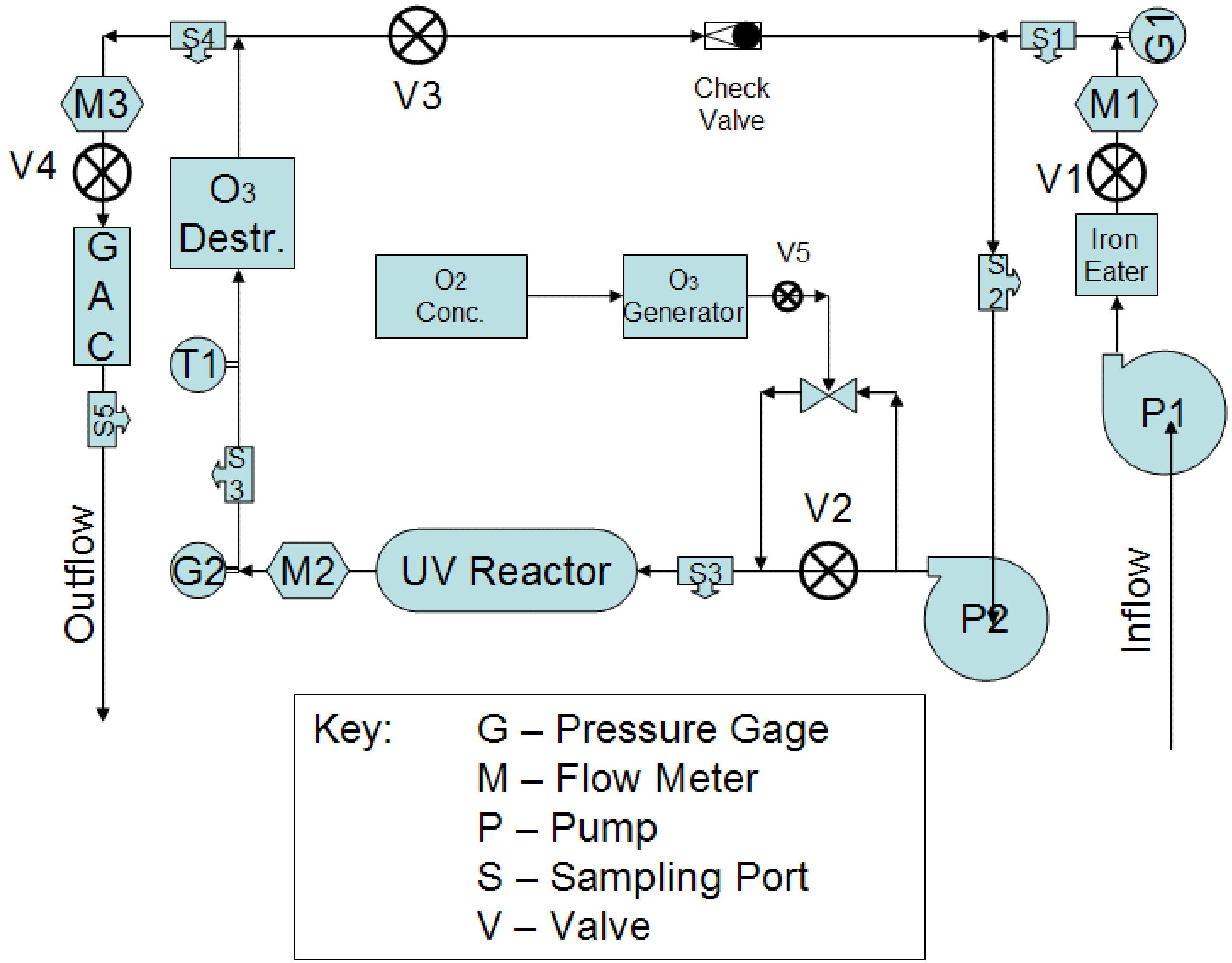
Sample Collection

Sample Collection



AOP Field Equipment

AOP Schematic Diagram



Experimental Design

- MTBE: 30 - 300 ppb
- AOP Treatment:
  - Q = 1, 2, 3 gpm (t_d = 3.0, 1.5, 1.0 min)
  - R = Q_r/Q = 2.9 – 8.5
  - Frequency: 0, 30, 60, 90, 120 min

Mean Inlet Organic Properties (ppb)

TBA	TBF	Ac	IPA	MTBE	MAc
129	ND	3	7	182	ND

B	T	E	X
15	1	1	1

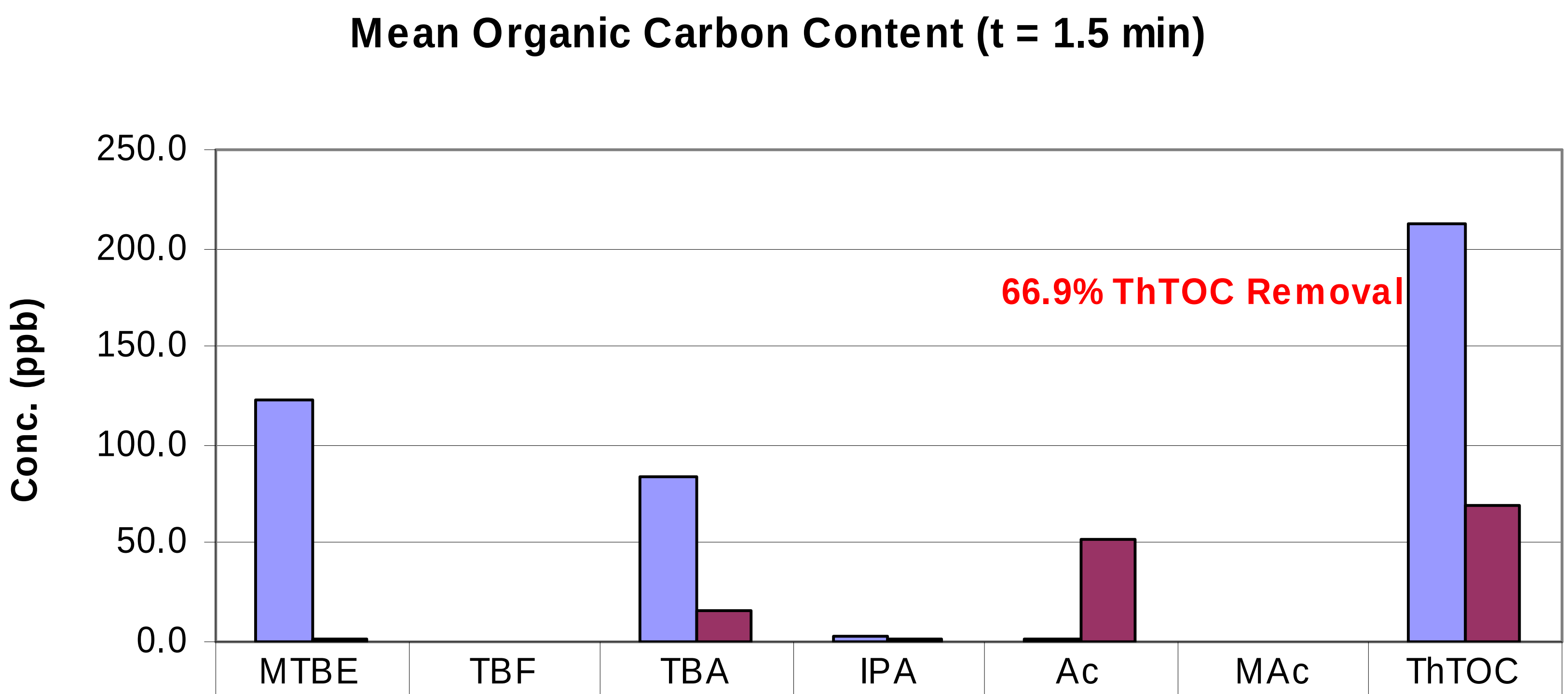
TOC
303

Mean Organic Removal

	TBA	TBF	Ac	IPA	MTBE	MAc
In	129.0	ND	3.0	7.0	182.0	ND
Out	25.4	0.2	85.9	1.7	2.3	0.9
Eff.	80	-	-2762	76	99	-

Note: BTEX removed to below detection level (100% removal)

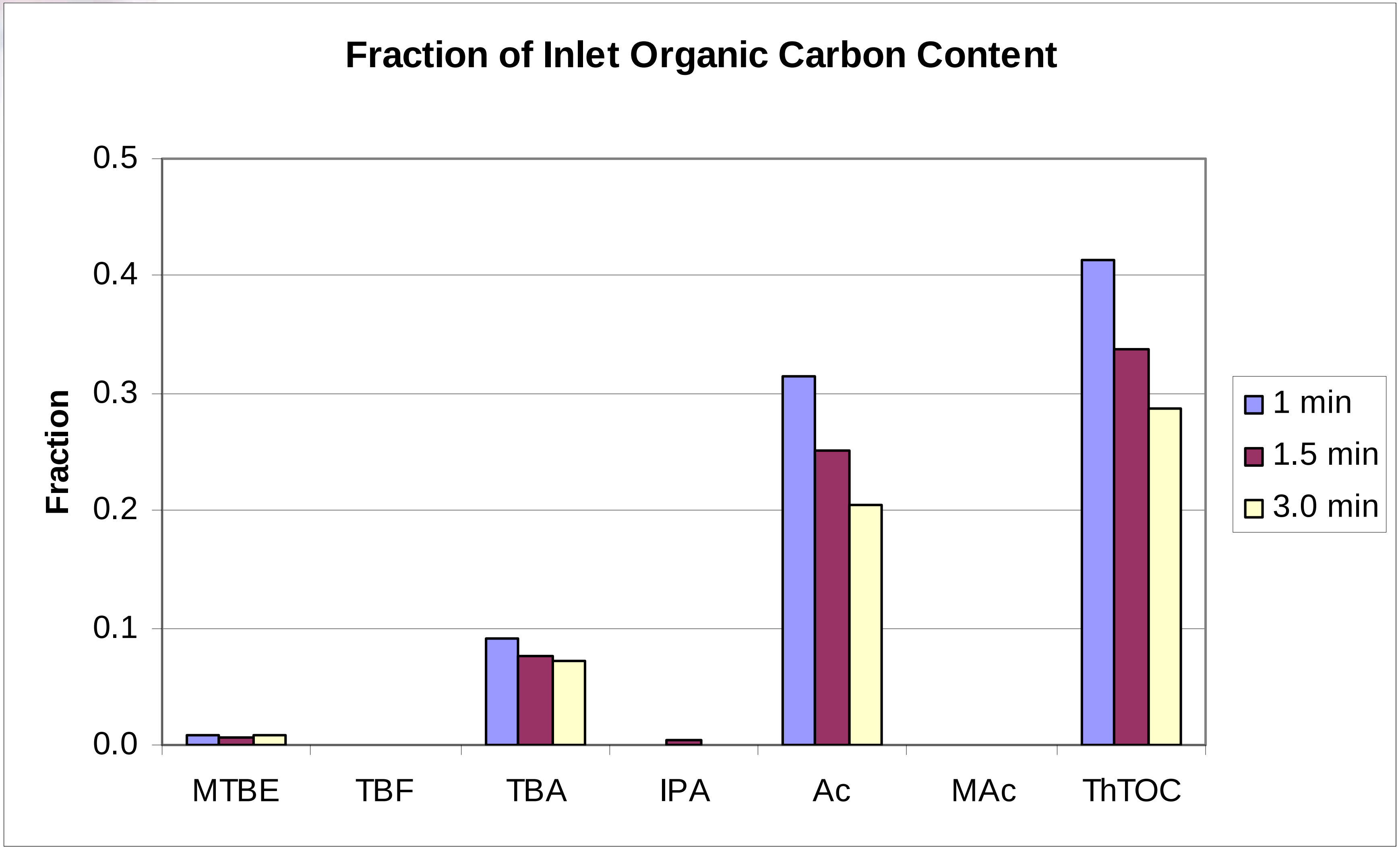
Contaminant Removal



	MTBE	TBF	TBA	IPA	Ac	MAc	ThTOC
Inlet	123.0	0.0	83.9	3.0	2.0	0.0	211.9
Oultet	1.4	0.0	15.6	0.9	52.0	0.2	70.0

Organic Compound

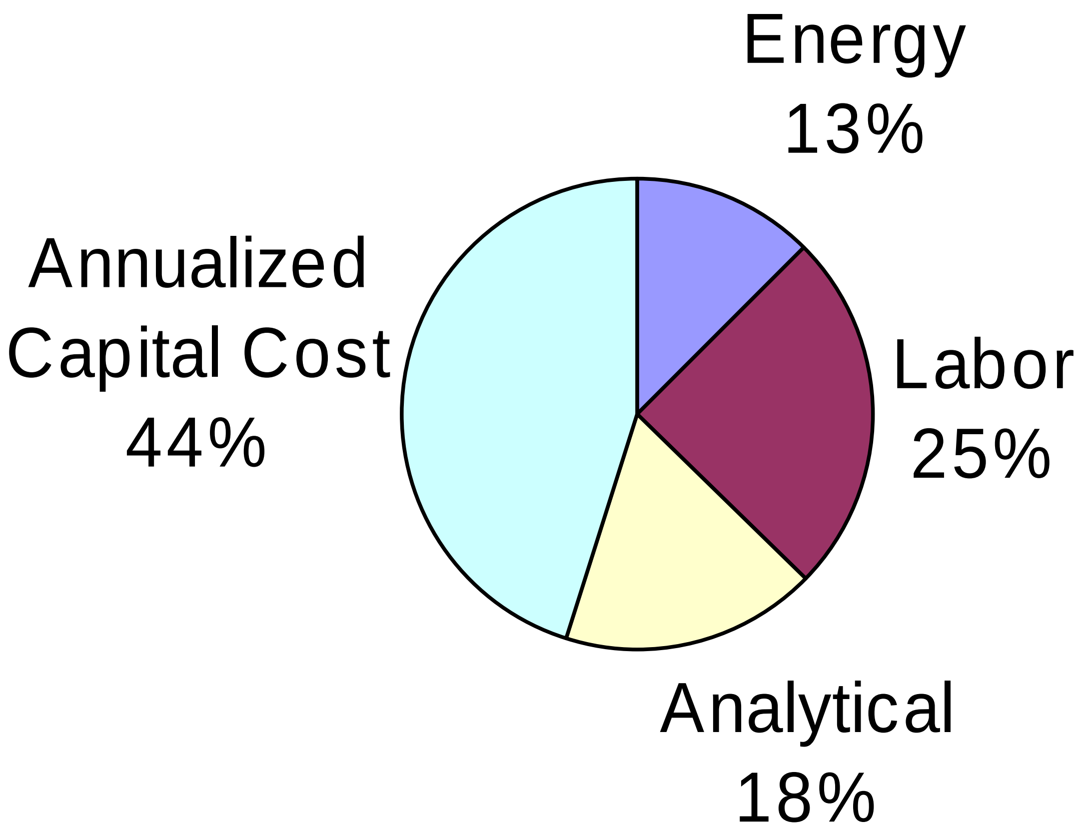
Fate of Organic Compounds



Annualized Economics

Item	*Annual Cost*
Energy	$1,341
Labor	$2,640
Analytical	$1,920
Annualized Capital Cost (6%, 10 Yr)	$4,818
Total Annual Costs	$10,719
Volume (1,000 gal/yr)	1,577
Total Annual Unit Cost ($/1,000 gal)	$6.80

Cost Distribution



Conclusions

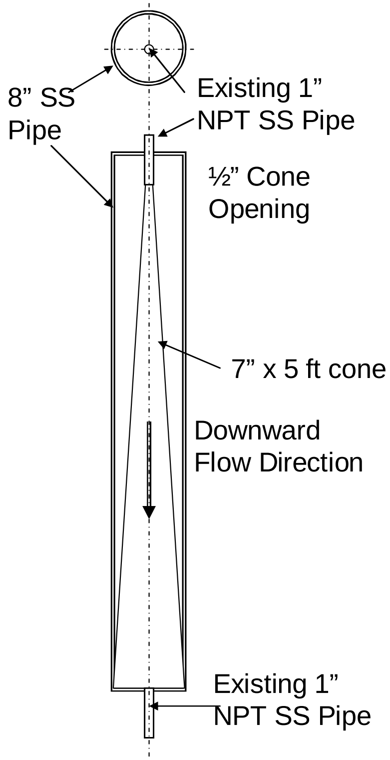
- AOP breaks down MTBE, TBA at efficiencies of about 90, 80% at t_d between 1 and 3 min.
- The main organic oxidation byproduct is Ac. Ac increases from ND to about 25% of ThTOC
- Minor improvement observed in MTBE and TBA removal by increasing t_d from1 to 3 min
- Ac removal is enhanced with t_d

Conclusions

- Total unit cost (TUC): $6.80/1,000 gal
- Energy represents only 13% of total cost. Capital replacement is 44%. Thus, TUC may be decreased as technology is more widely accepted; thus reducing manufacturing costs

Future Research

- Increase O_3 solubility using a Speece Cone Diffuser
- Target Acetone removal:
  - Improve UV light efficiency
  - Increase retention time



Acknowledgments

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