Impacts of Acetone and 2-Butanone Generation in VOC Sampling in Remedial Action Compliance

Presented by

Jackson Kiker (ECC)

Email: Jkiker@ECC.net

Negative Impacts of Methyl Ketone Detections

- Falsely attributed to site contamination or to a source release
- Methyl ketones pervasive VOCs
- Overall Data Quality perceived as poor
- Additional studies / comment responses to regain community confidence
- Review of Studies on Methyl Ketones for a Resolution to these issues

Regulatory Community Concerns About Methyl Ketones

- Determine if 2-butanone is a environmental contaminant or a laboratory artifact.
- Address the acetone issue or assume all acetone sample detections are valid

Mitigate Costs and Restore Remedial Confidence

- To mitigate these threats to costs and confidence
  - Determine Methyl Ketone source
  - Determine representativeness of Methyl Ketones

Three Approaches to Determining Representativeness of Methyl Ketones

- Anthropogenic – Human produced and released Methyl Ketones
- Laboratory cross contamination
- Sampling Artifact
  - Biogenic – naturally or induced Methyl Ketone formation
  - Abiotic

Anthropogenic Sources of Methyl Ketones

- Anthropogenic – Human produced and released methyl ketones
- Acetone used in paint removers/nail polish removers
- 2-Butanone used in paints and adhesives

Laboratory Sources of Methyl Ketones

- Laboratory Cross Contamination
  - Solvent used for glass washing
    - Detected in tripblanks
    - Detected in method blanks
    - Detected in field blanks
  - 2-Butanone not a common laboratory solvent

Biogenic Sources of Methyl Ketones

- Biogenic – formation by microbes or plants
- Plants; White clover, Ponderosa Pine[1]
- Microbes; Vibrio Species – Leucine Catabolism[2,3];
- Microbes: Decarboxylation of acetoacetate in clostridia[4]
- Microbes: Methane and MeOH grown Methylotrophs[5,6]

Microbial and 5035 Study Limitations

- Referenced studies were not performed for 5035 validation
- Concerned with microbial metabolism pathways or atmospheric VOC loading
- 5035 studies focused on effect of preservative and optimization but not on cause

Big Picture

- Use the results of microbial studies and 5035 studies to in relation to site conditions to evaluate probable cause of acetone and 2-butanone detections.
- Elimination of acetone and 2-butanone as site constituents of concern

Studies Evaluated

- MMR Soils in “Acetone Production as a Result of Sodium Bisulfate Preservation Using EPA Method 5035[7]”
- Sediments in “Microbial Oxidation of Gaseous Hydrocarbons: Production of Methylketones from Corresponding n-Alkanes by Methane Utilizing Bacteria[6]”
- Field Sample Data from Site 02 NAS Brunswick

MMR Soils[7]

- Acetone and 2-butanone detected in soils
- Significant correlation between acetone levels and organic carbon content
- Significant correlation between acetone levels and elapsed time before analysis (ie. Reaction time)
- MeOH and Sodium Bisulfate preservatives in organic soils yielded acetone
- Biotic or abiotic pathway not determined

Studies of C-1 Utilizing Methylotrophs[6]

- Obligate and facultative methane (C-1) utilizing bacteria obtained from soil and lake water
- Microbes grown on Methane and Methanol
- Harvested cell suspensions of obligate and facultative microbes oxidized butane and propane respectively to 2-butanone and acetone

Experimental Conditions[6]

- Cell suspensions (0.5 ml) placed into 10-ml vials with 50 mM sodium phosphate buffer (pH 7.0)
- Vial headspace removed and replaced with gaseous n-alkane substrate (propane or butane) or liquid substrate (pentane or hexane)
- Vials incubated at 30^{o} C and shaken
- Oxygen added in a 1:1 volumetric ratio

Experimental Results[6]

- Heat killed cells did not catalyze oxidation of n-alkanes to their corresponding methylketones
- n-Alkanes were not oxidized under anaerobic conditions
- Formation of primary and secondary alcohols detected as intermediates to methylketone

Experimental Results[6]

- Relative rate of formation;

  Acetone>2-butanone>2-pentanone>2-hexanone
- Factors affecting methylketone production
  - Time
  - Cell mass
  - Temperature (maxima at ca. 30^{o} C
  - pH (maxima at ca. 7.0)
  - Metal chelating agents inhibited oxidation
  - Required oxygen atmosphere

Methylketone Microbial Formation Conditions

- Methanogen Microbial evidence
- Organic carbon precursors
- Exposure to oxygen
- Geochemical conditions favorable for methanogens and organic carbon breakdown

Organic Carbon Precursors for C1 Utilizing Microbial Pathway[6]

- Propane - oxidized to its methylketone; acetone
- Butane – oxidized to its methylketone; 2-butanone
- Sources biogenic or thermogenic organic carbon decomposition

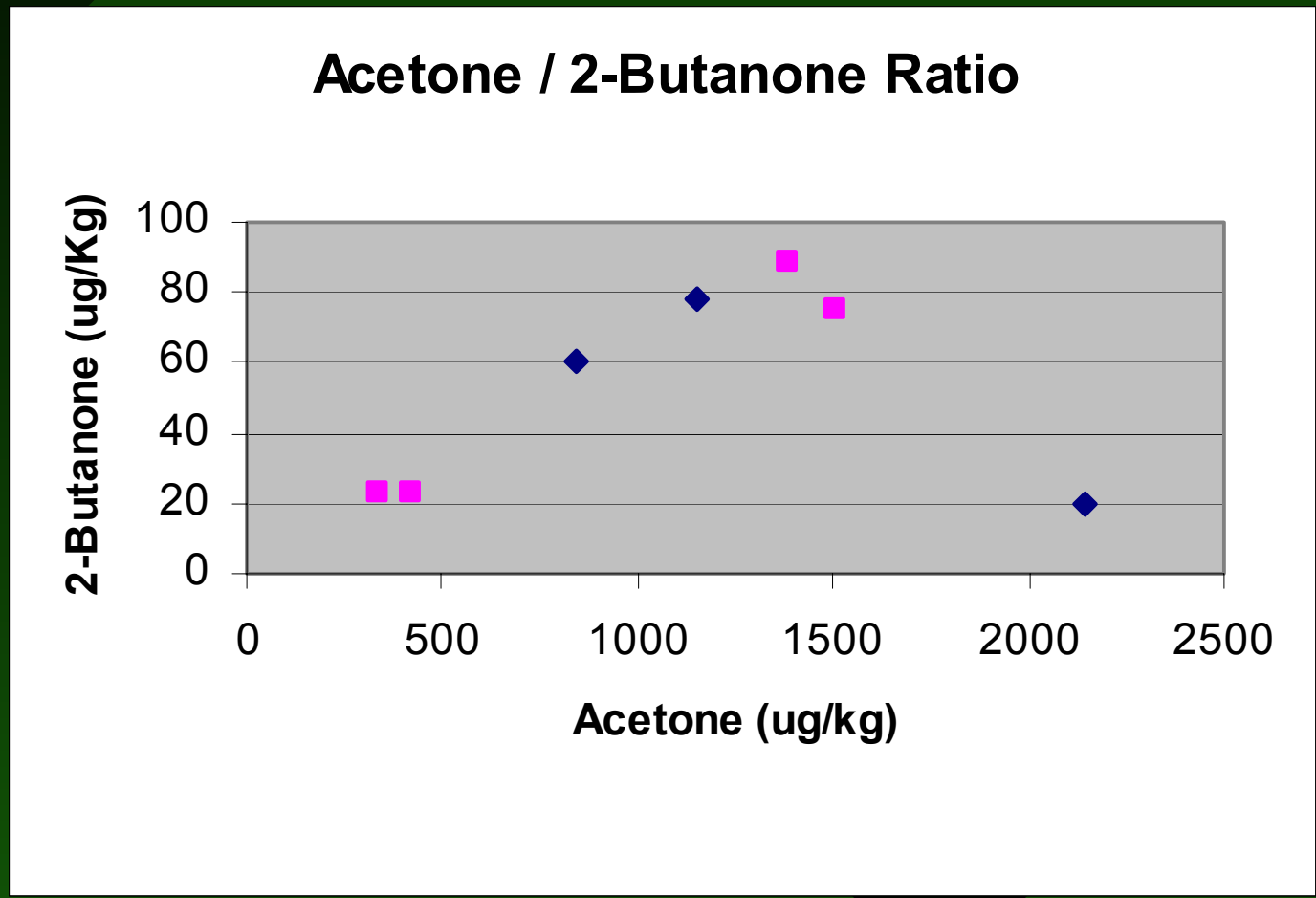
Site Conditions

- Wetland bogs
- High TOC > ca. 10,000 mg/kg
- Percent solids ca. 20%
- Methane detected in co-located groundwater
- ORP and DO low in co-located groundwater

Acetone and 2-Butanone Site Detections

- Acetone detected in site waters at low levels compared to sediments
- 2-butanone not detected in site waters
- Acetone levels in sediments ca. >300X greater than site waters
- Site water detects sporadic event to event and do not delineate a plume

Site Methylketone and Acetone/2-butanone Ratio



Summary

- In addition to studies showing Sodium Bisulfate and MeOH effects on methylketone levels - a microbial mechanism for high organic soils may be possible
- Possible microbial methylketone reaction pathway – preferential oxidation to methylketones and in anticipated biogenic alkane ratios
- Acetone and 2-Butanone detects can be defended as not representative of site conditions and viewed as a sampling artifact
- Microbial mechanism; then freezing and elimination of oxygen headspace to minimize methylketone formation

References

- C. Potter et al, 2003: Modeling Terrestrial Biogenic Sources of Oxygenated Organic Emissions. *Earth Interactions,* **7,** paper No. 7, 1-14.
- R. Fall et al, 1999: Acetone Formation in the Vibrio Family; a New Pathway for Bacterial Leucine Catabolism. *J. Bacteriology,* **181,** pg 7493-7499.
- R. Fall et al, 1995: Marine Vibrio Species Produce the Volatile Organic Compound Acetone. *Applied and Environmental Microbiology.* **61,** pg 44-47.
- P. Soucaille et al. 1998: Regulation of Solvent Production in Clostridium Acetobuylicum. *Trends Biotechnol,* **16,** pg 11-16.
- R. Patel et al. 1980: Microbial Oxidation of Gaseous Hydrocarbons: Production of Methylketones from Corresponding n-Alkanes by Methane-Utilizing Bacteria. *Applied and Environmental Microbiology.* **39,** pg 727-733.
- C. Hou et al. 1979: Microbial Oxidation of Gaseous Hydrocarbons: Production of Methyl Ketones from Their Corresponding Secondary Alcohols by Methane- and Methanol-Grown Microbes. **38**, pg 135-142.
- J. Clausen et al. 2000: Acetone Production as a Result of Sodium Bisulfate Preservation Using EPA Method 5035. 16th Annual Conference on Contaminated Soils at Univ. Massachusetts.