Next Generation Ambient Air Monitoring for Benzene and Toluene Compared with Traditional Methods at the Fenceline of an Indiana Oil Refinery

Motria Caudill¹, Wayne Whipple¹, Karen Oliver², Donald Whitaker²

¹EPA Region 5, ²EPA Office of Research and Development
Significance

- EPA’s National Air Toxics Assessment (NATA)\(^1\) shows benzene is one of the two top contributors to overall cancer risk in the U.S. from inhalation exposure.
- Toluene is a neurotoxin and an important tracer for mobile sources and industrial emissions.
- Air monitoring for VOCs is relatively expensive, because of required infrastructure and highly-skilled laboratory services.
- Highest benzene concentrations near industrial sites, most notably coke ovens & petroleum refineries.

Additional emissions control requirements
Application of a new air monitoring method to detect fugitive emissions
EPA set an annual average benzene concentration standard at the refinery fence line, measured using 2-week integrated samples placed around the refinery fence line perimeter.

*Does the proposed monitoring method compare well with current procedures?*
EPA’s current method – 24-hr canister sample, TO-15 in lab

Used in the National Air Toxics Trends Station (NATTS) network

GC-MS
Alternative to current method – Hourly data in field via autoGC

Used at Photochemical Assessment Monitoring Stations (PAMS) sites
Proposed method – Passive tubes, collection via Modified Method 325A, analysis via Modified Method 325B

Thermal Desorption (TD) -GC-MS
This study

- Follow-up to an initial feasibility study led by EPA’s Office of Research and Development (ORD) and Regions 3, 5, 6, & 8: “Collaborative Evaluation of a Low-Cost Volatile Organic Compounds Passive Sampling Method & Analytical Laboratory Intercomparison”.

- Our objective is to quantify the comparability of the new passive tube method to EPA’s recommended method for VOC sample collection – canisters.

- Added benefit: we received permission to piggyback sampling on an existing fenceline network of autoGC stations at an Indiana refinery.
BP Refinery, Whiting, Indiana

- Four-station fenceline network is result of 2012 agreement between refinery, regulators, & private citizen groups.
- BP committed to provide comprehensive air quality information regarding conditions at the fenceline via this public website:

  http://raqis.radian.com/pls/raqis/bpw.whiting
We collected 8 sets of 1-week samples on top of GC trailers.
Challenges – logistics

- Scientists not accustomed to extensive safety and security procedures at a refinery
  - Field staff underwent safety training
  - Fire retardant suit, reflective vest, hardhat, protective gloves, etc.
- Check in/out at each sampling location
- Everything took longer than expected
- First sampling event incomplete due to rain and risk of lightning. Several hours under “stop work” orders for outdoor activities.
Challenges – technical

- EPA-CRL provided canisters under vacuum
  - passive flow regulators on inlet, set to fill in 7 days
  - if canisters fill too quickly, they equilibrate with environment and gases diffuse in/out
- EPA-ORD provided multiple tubes each week
  - blanks & duplicates, shipped overnight in coolers
  - 2-week sampling in proposed rule
  - only 1-week sampling feasible with available canisters
Challenges – data comparison

- BP posts 1-hour data on public website
  - 168 measurements per week if all reported
  - about 25% missing values & up to 40% nondetects
  - hourly data were averaged to match week of passives

- All participants reported different VOC list
  - CRL determined 60 analytes in canisters
  - ORD determined 9 in tubes
  - BP determines 4 via autoGC
  - only benzene and toluene on all lists
Results

- 28 valid sets (of possible 32) 1-week paired canisters & tubes collected; analyzed at CRL and ORD, respectively

- Comparison methods
  - Plotted linear regression for full dataset
    - Correlation (R-squared), intercept, and slope
  - Calculated Relative Percent Difference (RPD) for each pair

\[
\% \text{RPD} = \left(\frac{C_1 - C_2}{C_1 + C_2}\right) \times 100\%
\]

U.S. Environmental Protection Agency
Benzene – Canister and Tube Results

U.S. Environmental Protection Agency
Benzene – Canister vs. Tube Regression

\[ y = 0.9333x + 0.0695 \]

\[ R^2 = 0.4872 \]
Toluene – Canister and Tube Results

Sample set, Week-Site

Concentration, ppbv

U.S. Environmental Protection Agency
Toluene – Canister vs. Tube Regression

\[ y = 0.7155x + 0.2066 \]
\[ R^2 = 0.5858 \]
Benzene and Toluene – Canister vs. Tube RPD

25% target for air toxics
Toluene – Canisters & Tubes Compared with hourly GC

\[ y = 0.7043x + 0.0554 \quad R^2 = 0.6863 \]

\[ y = 0.7973x - 0.0373 \quad R^2 = 0.7684 \]
Conclusions

- All three VOC monitoring methods compared within reasonable limits for both benzene and toluene.
- In general, the passive tube method resulted the highest concentrations and autoGC the lowest.
- More field testing is recommended to confirm that these relationships hold up during extreme summer and winter weather conditions.
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