COLORADO
Air Pollution Control Division
Department of Public Health & Environment

HB21-1189 Community Monitoring: Quarter 4 2023

Scope and Applicability

To fulfill the community monitoring requirements outlined in The Regulate Air Toxics Act (HB21-1189), the Air Pollution Control Division (APCD) Air Toxics and Ozone Precursors Program (ATOPs) utilized the Community Air Toxics (CAT) mobile laboratory in accordance with the state of Colorado, Department of Public Health and Environment (CDPHE) mission. The CAT was designed and developed by TofWerk and includes three instruments incorporated into a Mercedes Sprinter van for "real-time" measurement of ambient air while driving in communities. A duplicate of the CAT mobile lab, called the Emissions Monitoring Utility (EMU), was put into service on *December 8, 2023*.

The Colorado Regulate Air Toxics Act specifies monitoring of three toxic trace gasses (benzene, hydrogen cyanide, and hydrogen sulfide) in the communities surrounding four covered facilities to better understand how people in those communities are impacted by air quality. These air toxics are pollutants that are known or suspected to cause cancer or other serious health effects, such as reproductive effects or birth defects, or adverse environmental effects. HB21-1189 also directs Colorado's Air Quality Control Commission to identify additional covered air toxics over time. This mobile monitoring platform allows for measurement of hydrogen cyanide, hydrogen sulfide, benzene, and several "non-covered" volatile organic compounds (VOCs).

Method Overview

The CAT and EMU mobile laboratories both consist of two mass spectrometers and one optical spectrometer. Ambient air is introduced to the instruments through tubing on the roof of the van by an integrated mass flow controller. In addition, a MaxiMet weather station collects location, and meteorological data (temperature, pressure, wind speed and direction).

The Vocus Eiger Proton-Transfer Reaction Time-of-Flight Mass Spectrometer (PTR-ToF-MS) instrument operates using proton-transfer reaction mass spectrometry. This process uses hydronium ions (H_3O^+) to measure volatile organic compounds (VOCs). In the first step, the primary (or "reagent") ions react with trace gasses in air, ionizing them. The resulting analyte ions are separated and quantified with a time-of-flight mass spectrometer.

The Vocus Aim Chemical Ionization Time-of-Flight Mass Spectrometer (CI-ToF-MS) instrument operates using chemical ionization mass spectrometry. This is a two-step ionization technique. In the first step, the primary (or "reagent") ions are made by illuminating a reagent gas stream with a vacuum ultraviolet lamp (VUV). The resulting ions are mixed with ambient air in a reaction cell. There, the reagent ions interact with trace gasses in air, ionizing them. The resulting analyte ions are separated and quantified with a time-of-flight mass spectrometer.

The Picarro Cavity Ring-Down Spectrometer (CRDS) analyzer uses light from a single-frequency laser that enters a cavity where three mirrors reflect the laser light. When the laser is on, the cavity quickly fills with laser light. A small amount of the laser light is transmitted through the mirror closest to the photodetector, which turns the incident light into a signal that is directly proportional to the light intensity in the cavity. As the light circulates in a cavity with a gas sample, the molecular absorption by the gas results in a decrease of the light intensity. Plotting the absorbance at each measured wavelength generates an optical spectrum. This spectrum contains absorbance peaks that are unique to each molecule in the sample. The height of a particular absorption peak is proportional to the concentration of a molecule that generated the signal.

CAT/ EMU Instruments	**Compounds reported**
Vocus Eiger PTR-TOF-MS	Benzene, Toluene, Xylene, Trimethylbenzene
Vocus Aim CI-TOF-MS	Hydrogen Cyanide (HCN)
Picarro CRDS	Hydrogen Sulfide (H_2S)

Quarterly Data Summary Notes for Q4 2023

Relevant links:

- Community Air Toxics Mobile Lab (CAT) Flyer
- Emissions Monitoring Utility (EMU) Flyer
- CDPHE- Regulate Air Toxics Act
- Stationary Wind data resources:
  - CDPHE Air Quality Dashboard
  - CDPHE Meteorology Data Selector Map

I. Limit of Detection and Method Detection Limit

Limits of Detection (LODs) were determined from auto-zeros the instrument performs during regular operation and these values change each time the instrument performs an auto-zero. LODs reported in the data summary are averaged quarterly from these moving LODs. All LODs used in flagging the data are reported on the "LOD" sheet. The reported Method Detection Limits (MDLs) were determined during the instrument audits. The table of LODs and MDLs for each compound and asset are reported on the Quarterly Summary tab of the Data Summary.

All LODs used to flag data are reported on the LODs tab. If the LOD is "nan" (or blank) for a given compound and timeframe, or if a given timeframe is missing altogether, then the MDL was used to flag the data instead. The "MD" flag was used to flag non-negative data that is less than the LOD or MDL. The moving LODs are computed as 3 times the standard deviation of auto-zeros that the instrument(s) perform during normal operation.

II. Computing Statistics

Data with the flag "BR" (indicating negative values) are replaced with zeros for computing statistics and non-zero data that are flagged "MD" are replaced with 0.5*MDL for statistics.

The quarterly pollutants stats table was computed at the end of the quarter for the specific region.

III. Instrument Time Delay

There are sampling time delays between the different instruments due to differences in sample line tubing length and sampling flow rates. Currently, this time delay is not corrected for in the quarterly data packets. These sampling delays were measured directly during the audits and were determined from bump tests at the inlet lines located at the top of the van.

CAT Instruments	Compounds reported	Time Delay of sampling (CAT)
Vocus EIGER PTR-ToF-MS	Benzene, Toluene, Xylene, Trimethylbenzene	6.5 seconds
Vocus AIM CI-ToF-MS	Hydrogen Cyanide (HCN)	7.5 seconds
Picarro CRDS	Hydrogen Sulfide (H_2S)	9 seconds

IV. Meteorological Data

A large amount of MetData has the flag “QW”, indicating questionable wind data.
When the vehicle is moving quickly and wind speeds are low, it can be challenging to accurately measure true wind.
Wind data are flagged if:

1. True wind cannot be distinguished from the wind generated by the vehicle’s motion while driving.
2. The difference between the wind speed (direction) and the vehicle’s speed (direction) is less than the error of the MaxiMet.

If the MetData are flagged “QW”, we encourage the user to use external sources to verify wind speed and direction:

CDPHE Air Quality Dashboard
CDPHE Meteorology Data Selector Map

V. GPS Data

Beginning in Q3 of 2024, new procedures were implemented for quality-correcting and post-correcting GPS data. When possible, incorrect GPS points were post-corrected by snapping their drifted location back to the deployment route and are flagged ‘CG’. Data points that are flagged only as ‘QG’ indicate that the point strayed from the deployment route, making the data point questionable. Data points that are flagged ‘QG’ and ‘AQ’ were nulled because the GPS location was too far from the standard route to confidently be post-corrected. Before Q3 of 2024, the GPS data is not post-corrected, and suspect GPS points were nulled.

VI. Quarter Specific notes

A. AIM Background Correction

An empirical background correction has been applied to all hydrogen cyanide (HCN) data to account for nonphysical discontinuities in mean HCN concentrations between different deployments. The background concentration is computed as the 5th percentile of the data from a given deployment. This background is then subtracted from all HCN data for that deployment and the data are then QC’ed as normal. Therefore, the reported HCN concentrations should be interpreted as enhancements above a background concentration, rather than absolute concentration measurements.