Method 327 Development – Fenceline for EtO and VC

David Berkowitz and Ned Shappley

USEPA OAQPS AQAD MTG

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Fugitives - Fenceline Measurement

Benefits from this approach

- Fenceline monitors are at ground level and capture VOC/HAP emissions emitted from fugitive sources (e.g., storage tanks, wastewater collection systems, equipment leaks, etc.).
- Most difficult to quantify using standard methods and make up the vast majority of emissions of VOC and HAP at chemical plants and refineries.

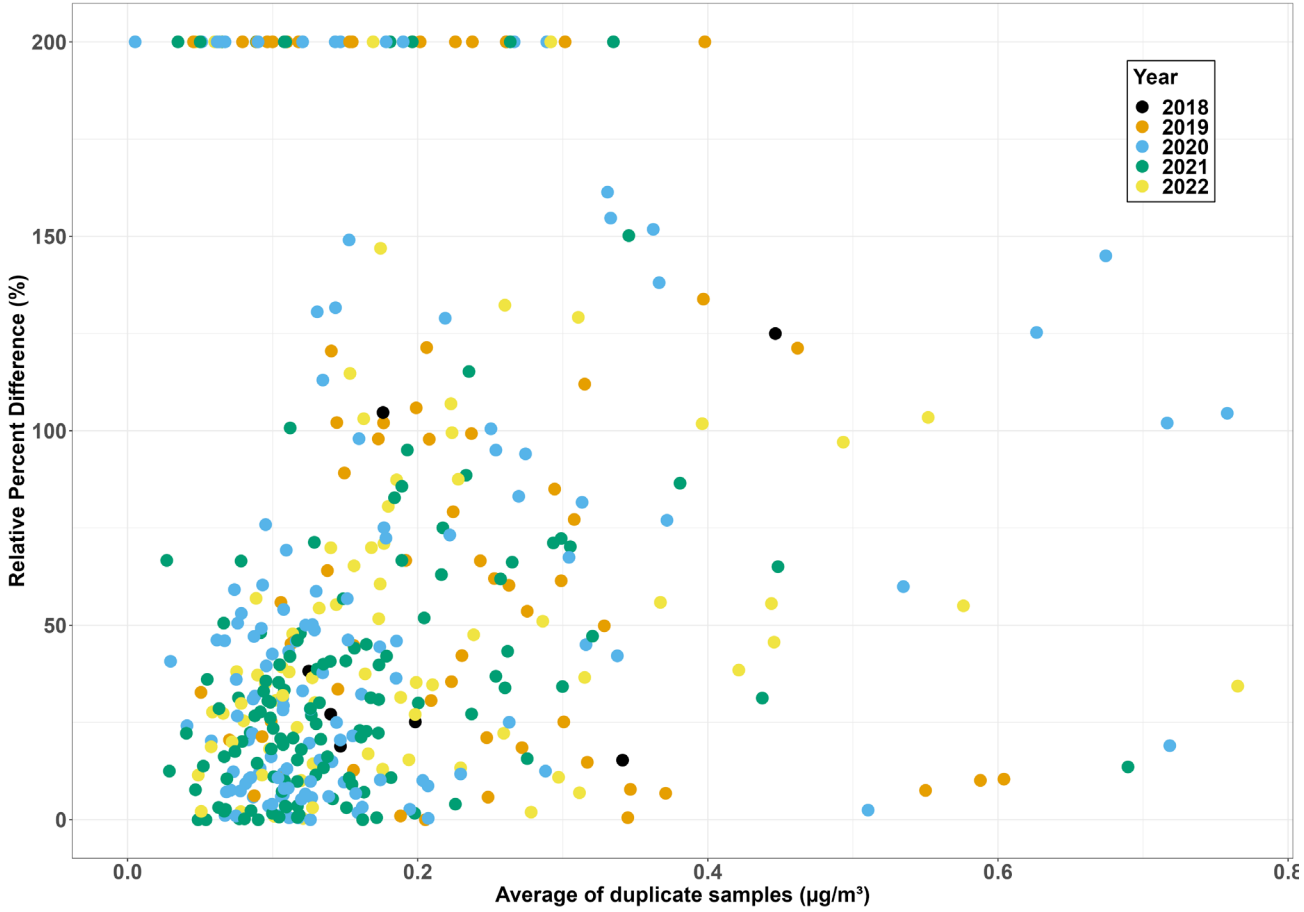
CAA Section 114 Testing Requirement for the chemical sector (i.e., HON)

- Fenceline Monitoring of EtO using an enhanced version of Compendium Method TO-15A
- Canister approach utilized for ambient sampling.

Canister Best Practices

- Material selection and cleaning requirements
- Hold Times
- Resolution Requirements

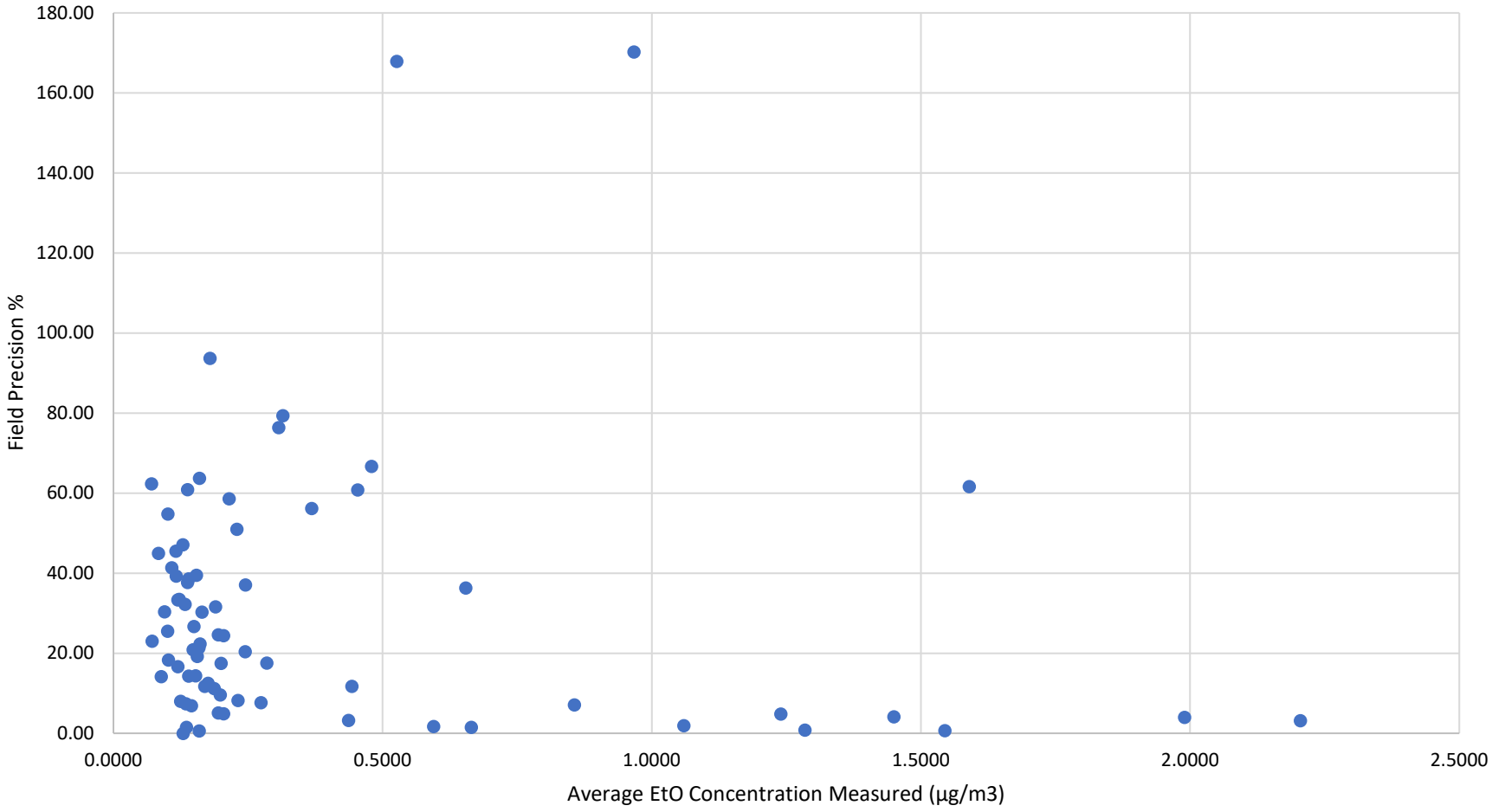
NATTS Laboratories EtO Duplicate RDPs by year



HON ICR – Fenceline Monitoring Precision

Memo : Representative Detection Limit (RDL) for Ethylene Oxide Using a Modified Version of Method TO-15A Memo (Garwood et al. EPA-HQ-OAR-2022-0730)

Figure 1. Field Precision as a Function of Concentration



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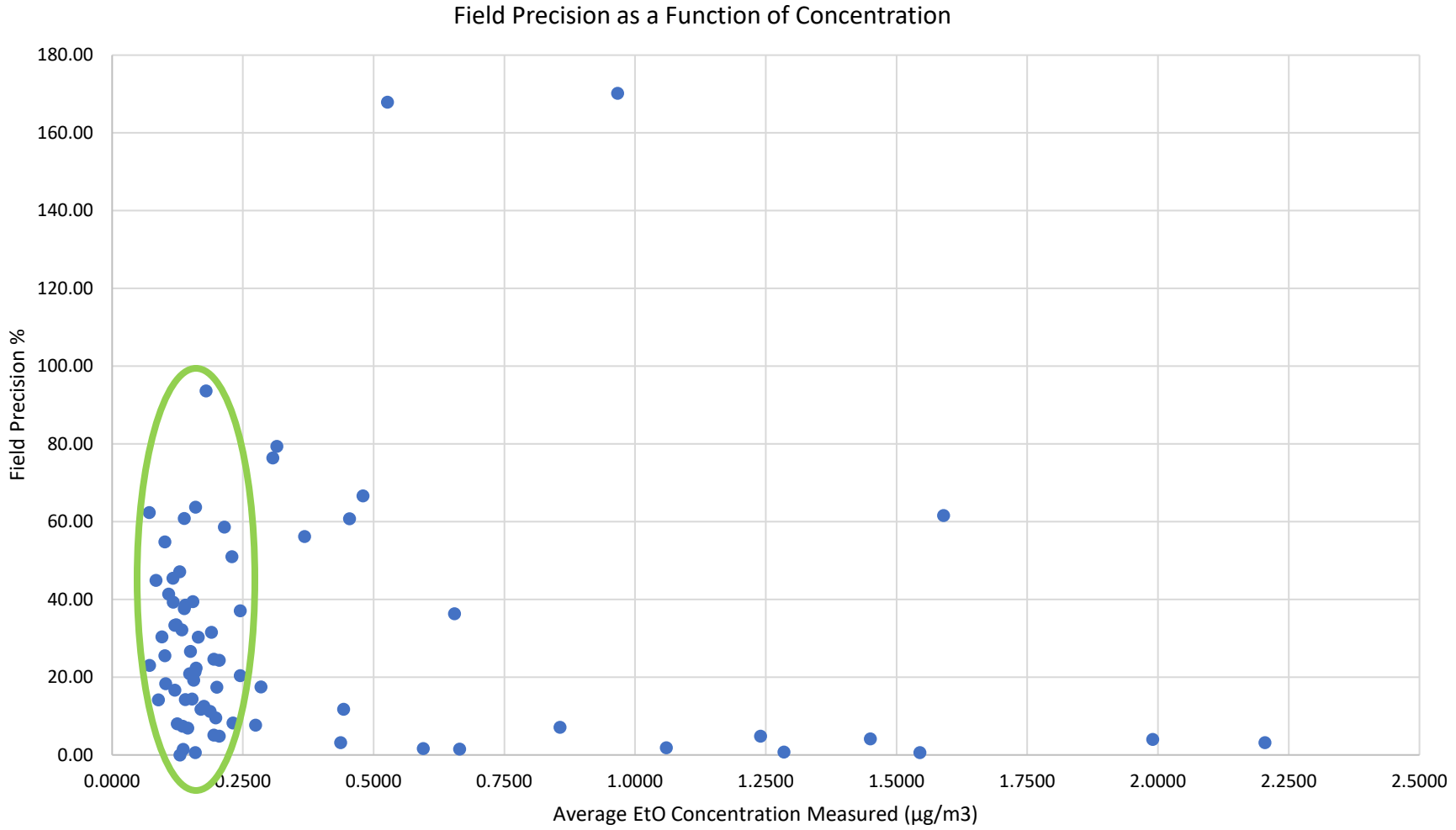

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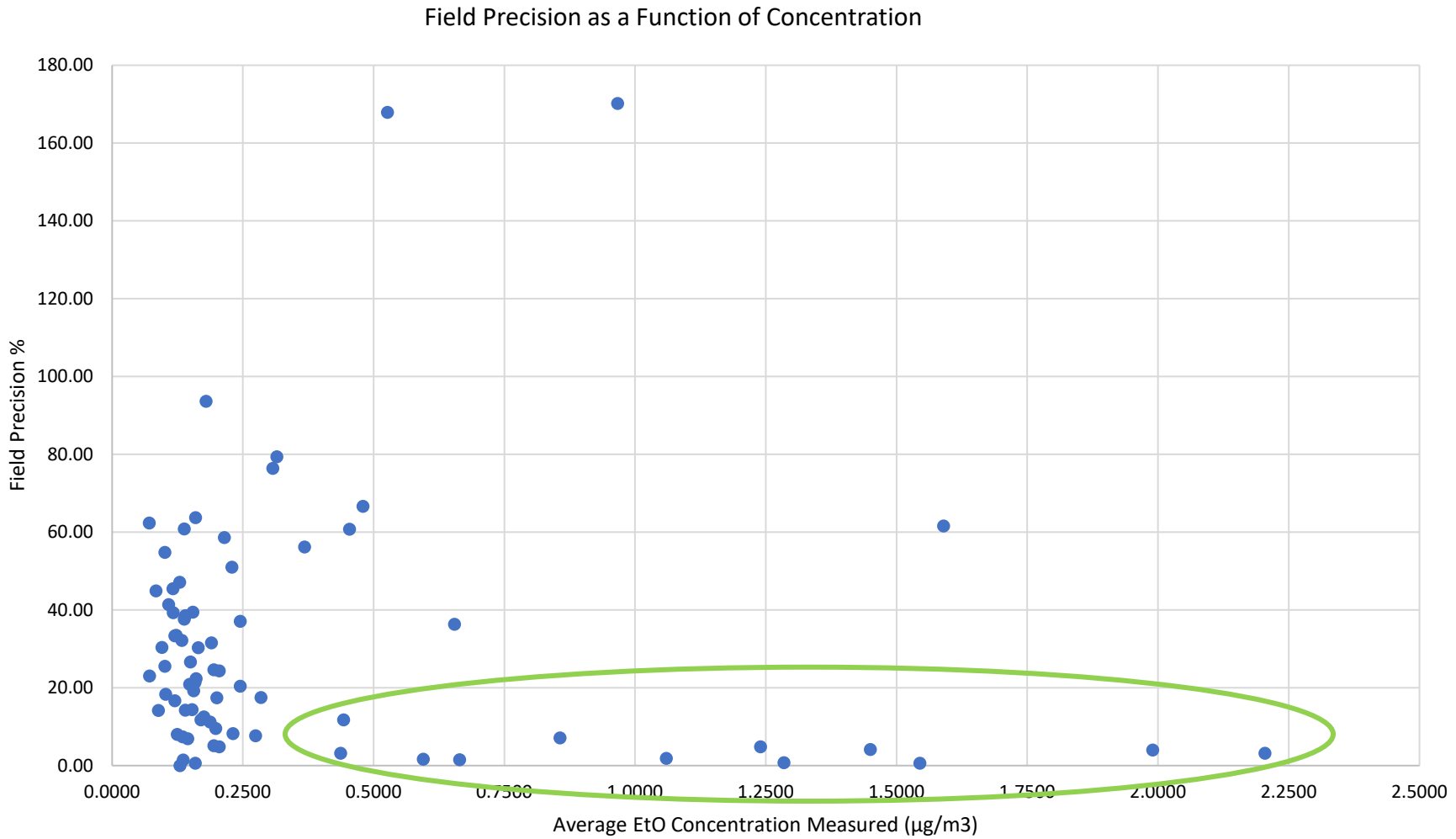

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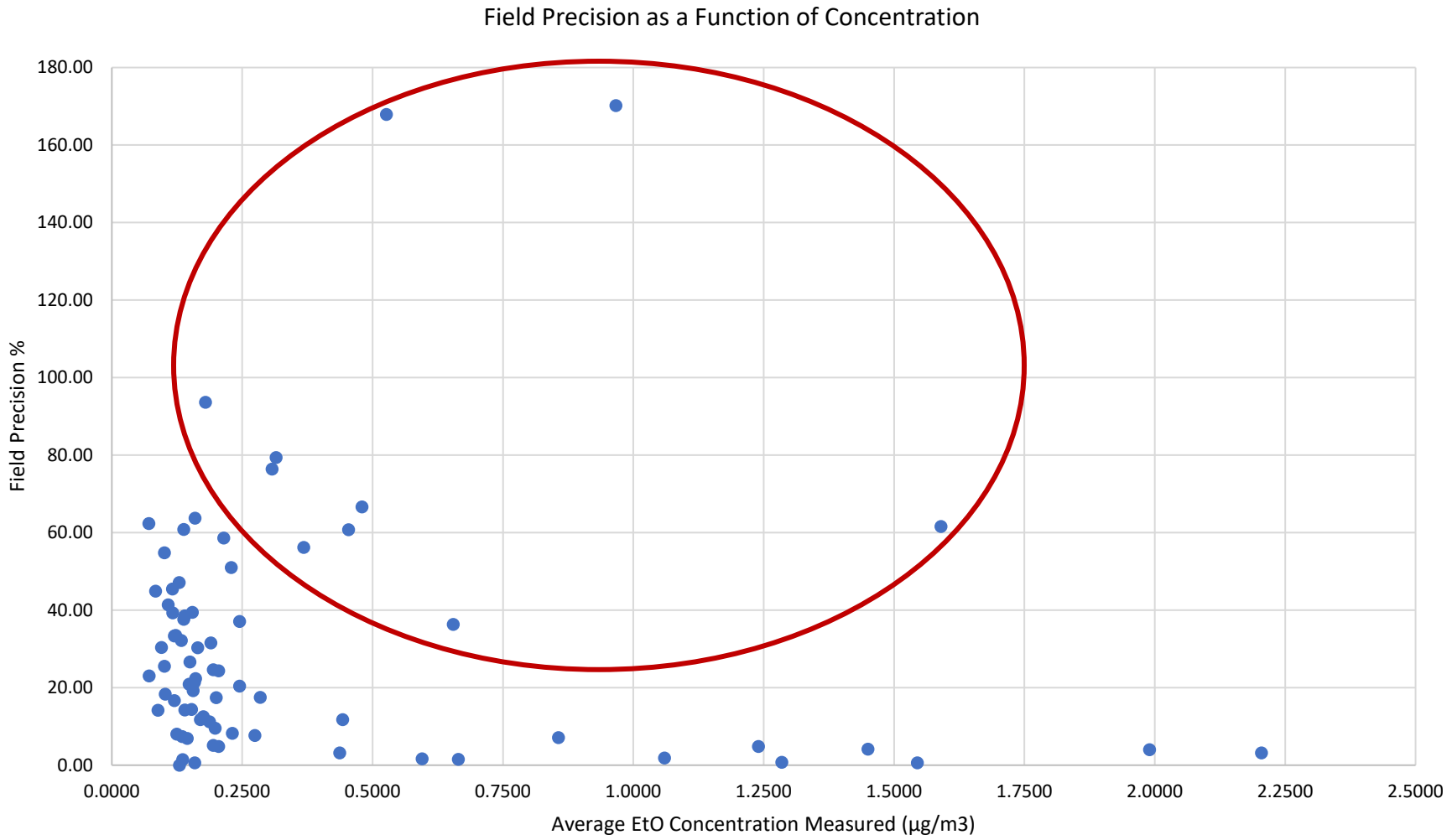


HON ICR – EtO Detection Levels

Memo : Representative Detection Limit (RDL) for Ethylene Oxide Using a Modified Version of Method TO-15A Memo (Garwood et al. EPA-HQ-OAR-2022-0730)

Summary of Field Blanks

Site Number	Field Tester Number	Lab Number	Sample Period	Result (µg/m3)
2	2	2	2	0.0144
5	2	2	4	0.0144
6	2	2	1	0.0144
7	2	2	4	0.0144
8	2	2	7	0.0144
9	2	2	1	0.0144
5	2	2	7	0.0170
5	2	2	1	0.0243
4	2	2	1	0.0347
1	1	1	4	0.0410
10	4	1	7	0.0410
1	1	1	3	0.0420
10	4	1	1	0.0420
1	1	1	2	0.0430
7	2	2	7	0.0466
8	2	2	4	0.0632
9	2	2	7	0.0725
4	2	2	4	0.0760

Summary of Reported MDLs

Site Number	Field Tester Number	Lab Number	MDL (µg/m^3)
1	1	1	0.048
2	2	2	0.030
3	3	1	0.050
4	2	2	0.029
5	2	2	0.025
6	2	2	0.025
7	2	2	0.025
8	2	2	0.025
9	2	2	0.025
10	4	1	0.050

Systematic Noise (SN) + Analytical Noise (AN) = Reasonable Detection Limit (RDL)

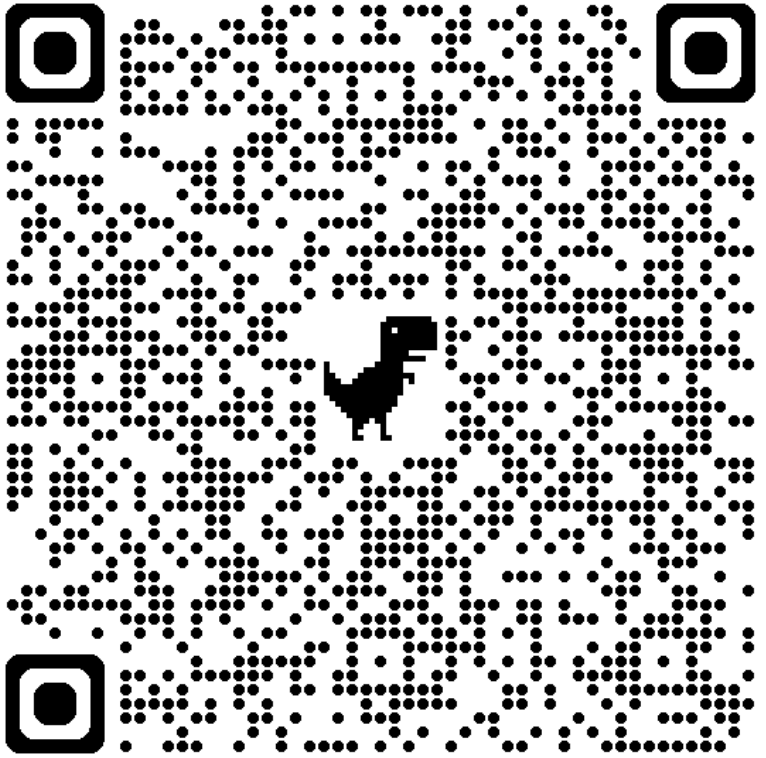
SN - 0.04 ug/m^3 + 0.03 ug/m^3 = RDL – 0.07 ug/m^3

Action Level = 3 x RDL or 0.20 ug/m^3

Hazardous Organic NESHAP (HON) Rule

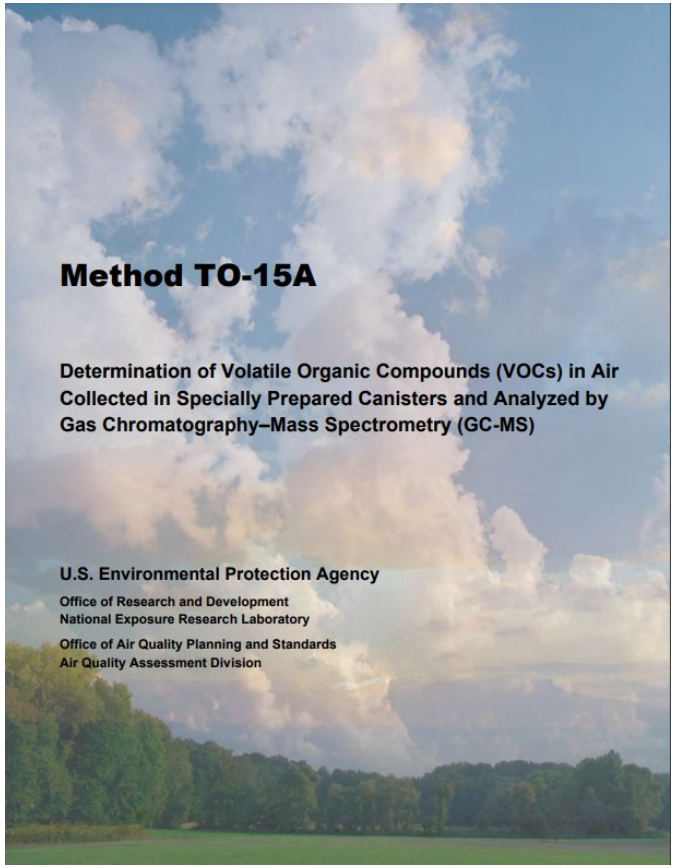
- Published in the FR on May 16, 2024
- Will reduce >6,200 tons/year of air toxics including EtO and Chloroprene
- Includes fenceline monitoring provisions for facilities that use, produce, store, or emit EtO, chloroprene, benzene, 1,3-butadiene, ethylene dichloride (EDC), or vinyl chloride (VCM).
- Biggest reductions in cancer risks to nearby residents will come from EtO reductions.
- EPA Method 327 written to support the rule with EtO measurements.
- 25+ facilities subject to Fenceline requirement in the HON and M327 sampling

FR Notice SOCMI-HON Rule



EPA Method 327

- Scope and Application: Sampling and analysis of emissions from fugitive and area sources to determine airborne concentration of selected volatile organic hazardous air pollutants (e.g., ethylene oxide or vinyl chloride).
- Method based on EPA guidance in Compendium Method TO-15A
- Applicability. The use of this method is strictly intended for determining airborne concentrations of selected speciated volatile organic hazardous air pollutants(oHAPs) in order to determine compliance with a fenceline emission standard and/or work practices when specified by the applicable regulation.



EPA Method 327

- Whole air sample collected using a particulate filter and flow control device into an evacuated, specially prepared canister
- Canister transported to the laboratory for analysis
- Sample directed from the canister into a pre-concentrator to collect speciated organic HAPs
- Analytical Approach: Gas chromatograph (GC) coupled with mass spectrometer (MS)

- **Key steps for sample collection: stringent leak testing, certified and clean canisters, certified sampling devices, field spikes, field blanks and duplicates**

- **Key steps for sample analysis: analysis of blanks, high-quality standards, method detection limit requirements, initial and ongoing calibrations and checks**

EPA Method 327

Field Sampling Performance Requirements

- Every twelve months
- Flow control verification: ensure constant flow rate for 24 hours and until 75% of canister volume is collected – every twelve months
- Flow control flow check: verify flow rate before and after each field sampling event
- Sampling device leak check: demonstrate leak-free before sampling
- Sampling device check: must be non-biasing under zero-air and known-standard conditions every twelve months.

Canister Performance Requirements

- Every eighteen months
- Canister design: minimum 6-liter, suitable for trace gas analysis, no prescription on material
- Leak check: annual qualification, pressure decay rate limit
- Zero-air verification: eighteen months, eight day hold, cleanliness analysis
- Known standard verification: qualification on an eighteen month basis, eight day hold, target analyte accuracy within ± 30%
- **Cleaning procedures and verification of cleanliness of every canister prior to sample collection**

EPA Method 327

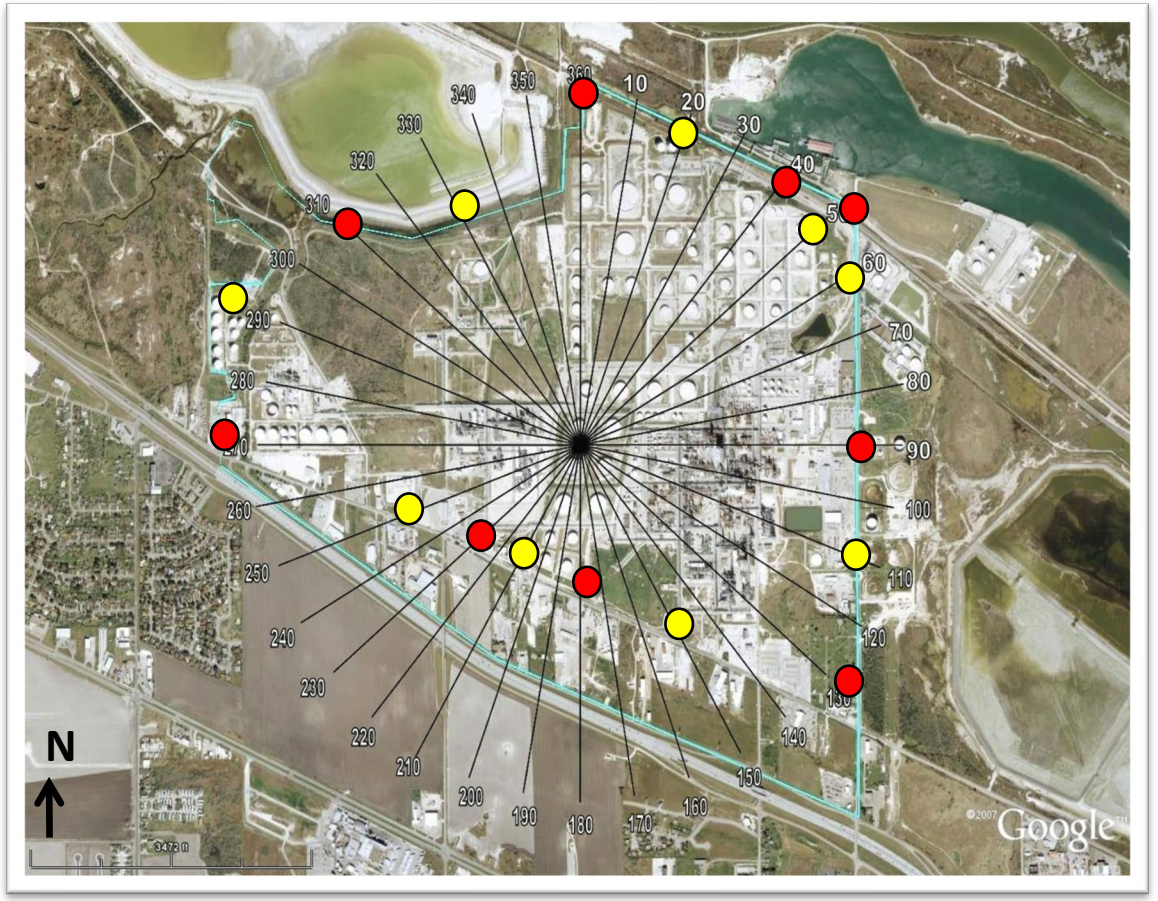
Example Analytical and Standards Requirements

- Analysis must be done within eight days
- NIST-certified or NIST-traceable gaseous standards
- MDL/LOD
  - Analyze under selected conditions with field used and cleaned canisters
  - Prepare/analyze 7 blank & spike samples (3+ batches/3 calendar dates)
- Ensure MDL/LOD of analytes <20 pptv & 1/10th of action-level concentration
- Samples quantitated using daily CCV standard.

Monitor Siting for Method 327 in HON

Fenceline Monitoring requirement in the HON NESHAP

- Method 325A approach for siting of monitors
- At least 8 sampling locations per sample day (1 in 5)
- Field blank and spike per monitoring event
- Rotate monitoring sites each sample day.
- Action-level based on an annual rolling average.
- Delta C (High Reading – Low Reading)



EtO Method Development

Ambient/Near Source

- Active sorbent tube
  - Gas Chromatograph-Electron Capture Detector (GC-ECD)
- Passive sorbent tube
  - Gas Chromatography/Mass Spectrometry (GC/MS)
- Real-time measurements
  - Preconcentration – Cavity Ringdown Spectroscopy (CRDS)

Stationary Source

- Impinger based sample collection
  - Gas Chromatography-Electrolytic Conductivity Detector (GC-ELCD) – Hall Cell

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About the Office of Research & Development

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David Berkowitz
919.541.4767
berkowitz.david@epa.gov

Questions?

EPA Method 327

EPA's Environmental Measurement Center