

AIR TOXICS THRU-THE-PROBE AUDITS

MDEQ – Air Quality Division
Air Monitoring Unit
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Michigan's VOC Network



- VOC samplers – Andersen AVOC using TO-15A. Samples for 24 hours, ending with + 20 pressure.
- Sampling frequency is 6-day for the Dearborn (NATTS) site and 12 day at the Detroit/SWHS site.

Michigan's Carbonyl Network



- Carbonyl samplers: Previously used in-house made but now using the ATEC M-100.
- Samples for 24 hrs at 750 ccm.
- Waters DNPH cartridges and Method TO-11A
- Dearborn (NATTS) and River Rouge site sample every 6 days. The Detroit/SWHS site is every 12 days.

Background – Toxics Audit Program

- Research and planning in 2003 to develop an audit program for VOCs and Carbonyls
- Utilized the California Air Resources Board (CARB) thru-the-probe (TTP) audit program, and modified this approach for Michigan's program.
- Equipment purchased in Spring 2004 and beta-testing was conducted in the Summer and fall of 2004.

Getting started....

- **2005** – Beta-tested the Thru-the-Probe approach at one site. Other checks done into the sampler's inlets.
- **2006**: Site modifications completed, Thru-the-Probe audits conducted
- **2007 – 2008**: Thru-the-Probe audits conducted.

Equipment

EnviroNics 2014 Gas Dilution System

- Programmable, contains compound library
- Operates in either “Flow Mode” or “Concentration Mode”
- Has a humidification kit for VOC – canister audits.
- 3 Flow controllers cc/min (10000,1000,150)
- Approximately 50 lbs
- Cost: \$25,000 (2004)

Equipment

Also needed:

- Zero Air generator, up to 25 psi
- High quality audit gas (VOC and Carbonyls)
- DI water for the VOC humidification column
- Teflon lines and fittings for Carbonyls
- Stainless lines and fittings for VOCs
- Regulator(s) for cylinder gases

Audit Gas Detail

MDEQ purchases 1 type of gas per calendar year to span 2 calendar years. (3rd and 1st quarters)

VOCs:

2005: Mix of low level compounds

2006 & 2007: Mix of 9 compounds all at 1 ppm (\$1300)

Carbonyls:

2005: Acetaldehyde 5.0 ppm

2006: Acetaldehyde 5.0 ppm (degraded in 2006)

2007 & 2008: Acetaldehyde 5.0 ppm (\$600)

EnviroNics 2014 Gas Dilution Unit



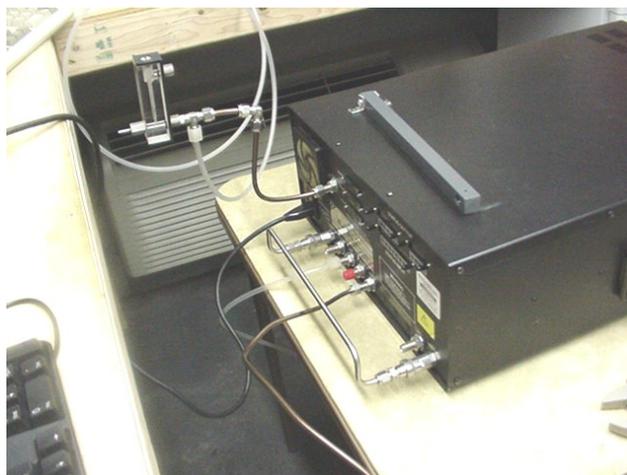
Probe Hook Up



Cylinder Gas and Zero Air Inputs



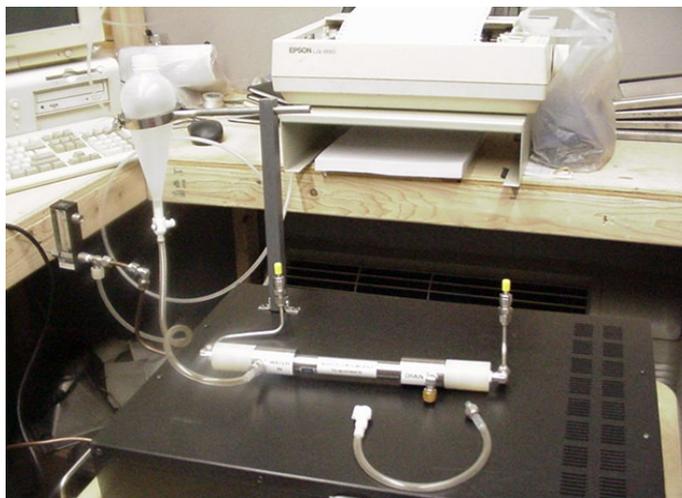
Gas and Zero Air Hooked up to EnviroNics



Environics ports



VOC audits – Humidification Kit



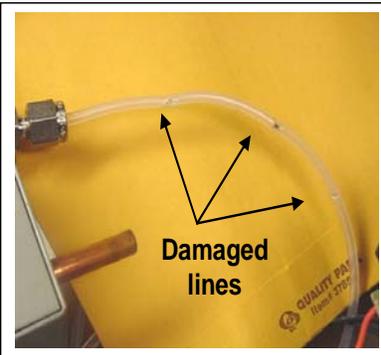
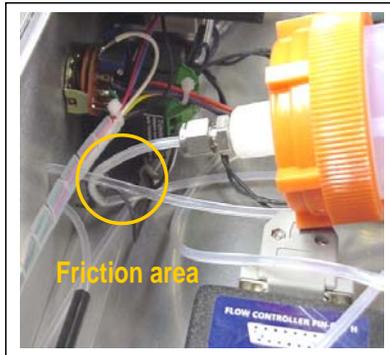
Results Carbonyls

- **2005:** Some sites into-the-sampler and some thru-the-probe (TTP). Both cases, results were close to target concentration.
- **2006:** TTP - Same tank as 2005, gas degraded but good precision site to site.
- **2007:** TTP- Close to target concentration
One site collocated – samplers not close
- **2008:** TTP- Close to target concentration
Again – collocated site not close, **discovered a leak inside one of the samplers**

Inside of the ATEC 100 Carbonyl sampler



Teflon line had splits from rubbing on other tubing inside the sampler



Results VOCs

- **2005:** Audits into the samplers, low level multi-gas gave mixed results, results sampler to sampler close for most compounds
- **2006:** Japan Mix (all compounds at 1 ppm) 2 audits into samplers others TTP. Precision sampler to sampler close. Not close to target – Environics not diluting properly due to a flow controller problem.
- **2007:** Same gas used as 2006, different mass flow controller used, close to target concentrations.

Lessons Learned

VOCs: Difficult to program when multiple compounds are at different concentrations. VOC audits take longer to set up due to using stainless lines and the humidification kit.

Carbonyls: Gas is not as stable as VOC mixes, but seems to be reliable within 6-8 month range rather than 10-11 months. Audits easier to set up with Teflon lines and no humidification column.

General: Takes time to work out the bugs! Challenges included; figuring out the correct flow and pressures settings, having excess flow was important, and identifying the flow controller and zero air pressure issues.

In Conclusion: The TTP audits are working, issues are being identified, and data quality is being improved.

Plans for the Future

I plan to upload 2007 audit data to AQS.

2008: Just finished carbonyl audits. Will order VOC gas in June and conduct audits in 3rd qt 2008 and 1st qt of 2009.

2009: VOC audits 1st qt. Will order carbonyl gas in June and conduct audits in 3rd qt 2009 and 1st of 2010.

As long as funding is available, will continue these audits.

Thank You.....Questions?

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