

# **Assessing Ozone Reactivity Emissions from a Biofilter at a Compost Facility Using the SCAQMD Modified USEPA Flux Chamber Technology and the UC Davis Mobile Ozone Chamber Assay Technology**

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## **INTRODUCTION**

A field study was conducted in order quantitatively examine the total non-methane non-ethane organic (TNMNEO) hydrocarbon emissions and ozone formation potential (maximum incremental reactivity) of air emissions from a biofilter control technology at a biosolids compost facility. The traditional SCAQMD modified USEPA surface emissions isolation flux chamber outfit for high advective flow sources was used to quantify the total non-methane non-ethane air emissions from the unit using the SCAQMD Method 25.3 for total VOCs, and then the exhaust gas from the chamber was tested using the UC Davis Mobile Ozone Chamber Assay (MOChA) for ozone formation potential or maximum incremental reactivity. The goal of the work was to examine the relationship between conventional ozone precursor emissions assessment and directly measured ozone formation potential. This is an important aspect of TNMNEO hydrocarbon or volatile organic compound (VOC) emission assessment regarding compliance of permitted sources since many hydrocarbon species emitted from compost site sources have low reactivity and thus result in lower effective ozone precursor emissions than accounted for by total VOC assessment technologies. Both VOC emission assessment data and incremental reactivity data will be presented, along with descriptions of the assessment technologies used.

## **METHODS**

Agencies in regions with severe air quality challenges, such as California's San Joaquin Valley (SJV), have raised concerns about volatile organic compounds (VOCs) or TNMNEO hydrocarbons emitted from complex sources which are suspected to contribute to persistent high levels of ground-level ozone formation. Agricultural and composting sources are prime examples of sources involving complex biology and chemistry that have recently come under scrutiny. The goal of this study was to characterize the reportable TNMNEO hydrocarbon emissions from a biofilter source and the ozone formation potential (OFP). By matching short-term OFP in the field (assessed with a mobile ozone chamber) to photo-chemically reactive

hydrocarbon compound assessment, we can better understand the significance of area source emissions in regard to regional air pollution concerns.

### **Total Hydrocarbon Emission Assessment**

Assessing flux from advective flow sources using the USEPA surface emission isolation flux chamber (flux chamber) introduces sample collection biases that are a function of the advective flow from the source<sup>2</sup>. The USEPA flux chamber technology was intended for diffusive flow area sources or very low flow advective sources where the volumetric flow from the source in the flux chamber are negligible compared to the method sweep air flow rate of 5 lpm. For high advective flow sources, the advective flow from the source negates the assumption that the flow from the source, compared to the recommended flow of sweep air of 5 lpm added to the flux chamber, is insignificant. In order to avoid this bias, a method modification has been adopted that uses a trace gas blend (10% helium and 90% ultra high purity air) as the flux chamber sweep air. The area source advective flow can be assessed by recovering the trace gas and calculating the advective flow from the source by the dilution of trace gas. Once the advective or volumetric flow of the source into the chamber is known, the flux is then calculated by including the advective flow term in the sweep air flow rate for a total volumetric flow thus preventing a bias in the assessment.

The need to assess flux from advective flow sources is found at compost facilities. SCAQMD Rule 1133.a describes using the USEPA flux chamber with a modified exhaust port and a trace gas as sweep air gas for assessing advective flow sources at compost facilities<sup>3</sup>. The tracer-dilution method, or the recovery of a known tracer in the flux chamber, can be used to assess the area source advective flow from an area source such as a static compost pile or a biofilter while the gas concentration of the source is being measured in the flux chamber for site assessment purposes. With the USEPA chamber design modified by using a 6" diameter exhaust stack in place of the standard 7/8" exhaust port, the flux of these advective sources can be assessed accurately without causing a 'back pressure' in the chamber, or a 'skirting' of source gas away from or around the chamber<sup>3</sup>. The recovery of the sweep air tracer provides the necessary information for the assessment. The advective flow into the chamber is measured by the recovery of the tracer and is then used in the calculation of flux from the test source. Samples collected from the flux chamber can be analyzed for project study compounds via regulatory approved analytical methods, or the exhaust gas from the chamber can be introduced into the MOChA and evaluated for ozone formation potential, or both.

### **Ozone Formation Potential Assessment**

Ozone is a secondary pollutant, arising from photochemical reactions between hydrocarbon (both natural and anthropogenic) and nitrogen oxides (NO<sub>x</sub>, which primarily arise from high-temperature combustion). One techniques used and reported in the literature is the MOChA combined with standard VOC or TNMNEO hydrocarbon measurement methods and compared through the use of photo-chemical model calculations<sup>1</sup>. In brief, we sample 1000L of source emissions, mix the source gas with standardized surrogate background gases (3 hydrocarbon compounds plus NO<sub>x</sub>) and subject to simulated mid-day solar illumination for 3-4 hours over which time ozone forms. This is a smaller chamber than typically used for atmospheric simulation, but the largest we could plausibly use meeting the portability needs of field work. This program included measuring the OFP from the exhaust gas of the USEPA flux chamber

modified for high flow sources and thus providing an assessment of the reactivity of the source emissions.

## **TECHNICAL APPROACH**

A site assessment was recently conducted at a biosolids compost facility complete with biofiltration in compliance with permitting requirements. The purpose of this testing effort was to conduct an evaluation of the air emissions from the biofilter using both the traditional, regulatory approved flux chamber assessment technology, and also with the MOChA for assessing ozone formation potential (OFP). The test objectives was to couple the assessment of these two technologies, and begin to generate a data base where hydrocarbon emission factors for area sources are also described by OFP. Project compounds were detected using: a real time screening (colorimetric detection tubes for ammonia), SCAQMD Method 25.3 for total non-methane non-ethane organic compounds (TNMNEOCs), and SCAQMD Method 207.1 for ammonia. A limited amount of hydrocarbon speciation was also conducted using the USEPA Method TO-15.

The testing included assessing emissions from two cells in the biofilter unit using the SCAQMD Modified USEPA surface emission isolation flux chamber (flux chamber) technology. Three points were measured on each surface that were randomly selected. In one of the flux chamber locations, exhaust gas from the chamber was withdrawn and input into the MOChA for OFP assessment. In addition, the biofilter was tested prior to the joint testing effort using the MOChA.

Sampling for ammonia emissions was performed by acid impinger sampling collection, and analysis was performed off site by modified SCAQMD Method 207.1 utilizing ion selective electrode. Sampling for hydrocarbon emissions was performed by cold trap and vacuum tank sample collection. The analysis was performed off site by SCAQMD Method 25.3 for TNMNEO compounds utilizing combustion/infrared Total Organic Carbon (TOC) analysis for the trap and FID detection for the tank. GC/thermal conductivity analysis was also performed on the tanks in order to assess fixed gases including carbon monoxide, carbon dioxide, and methane.

## **QUALITY CONTROL**

Control procedures that were used to assure sufficient data quality for the testing effort including laboratory method quality control protocols, field replicate testing, field blank testing, and adherence to flux chamber protocol as described in the USEPA User's Guide and as applied by SCAQMD Rule 1133 for assessing biofilter inlet and surface emissions.

## **RESULTS**

All emissions calculated from the biofilters were made using the average flux chamber concentration multiplied by the duct measured (SCAQMD Method 1 and 2) biofilter inlet flow rate (84,000 cfm). Table 1 summarizes the results obtained during this test for ammonia, carbon monoxide, carbon dioxide, methane, and total hydrocarbon compounds as THNMNEO compounds. Annual emissions were calculated by multiplying the daily emissions by 365 days for annual emissions. Table 1 also includes the results of the MOChA testing or ozone formation potential of the exhaust gas. The index for ozone formation potential was ranked as 'very low ozone formation potential', meaning that most of these TNMNEO hydrocarbon

emissions do not result in photochemical reactions that produce anthropogenic ozone in the atmosphere.

Table 1. Results of the TNMNEO Hydrocarbon/OFP Emission Assessments from the Biofilter.

Constituent	Average Concentration	Emissions	
	(mg/m <sup>3</sup> )	mg/min	tons/year
Ammonia	2.76	32,637	18.9
Carbon Monoxide	10.82	127,990	74
Carbon Dioxide	2407.78	28,469,193	16,496
Methane	9.73	115,085	67
TNMNOC	3.31	39,189	22.7
OFP	NA	Very Low	Very Low

## CONCLUSIONS

The methodology is available for assessing air emissions of total hydrocarbon compounds, ammonia, and other compounds of interest from high advective flow biofilters associated with the composting of biosolid materials. Assessment of the biofilter exhaust can be achieved using the SCAQMD Modified USEPA surface flux chamber and appropriate analytical methods; this approach produces data that are in compliance with historic permitting requirements and inventory needs. An assessment can also be made from these sources for ozone formation potential, which speaks to the effective ozone formation of the measured hydrocarbon emissions. It is apparent that, for this biofilter unit and process, most of the hydrocarbon compounds emitted from biofilter are not significant regarding ozone formation potential, which is the basis for the inventory assessment approach for reactive hydrocarbons. The low ozone formation potential can be supported by the analysis of the reactivity of the individual hydrocarbon compounds measured from the source. By combining these two assessment approaches, a link has been established for this type of area source where both the regulatory hydrocarbon emissions and ozone formation potential of those emissions has been established. Future studies will include building this inventory of hydrocarbon emissions and ozone formation potential to better understand the significance of area source emissions with regard to regional inventory regulations.

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## **KEY WORDS**

USEPA flux chamber, SCAQMD 1133, SCAQMD Modified USEPA flux chamber, dynamic flux chamber, TNMNEO flux, biofilter emissions, biosolids emissions, compost emission factors, ozone formation potential (OFP), MOChA

## **REFERENCES**

- 1) Kumar, Anuj, et.al., "Assessment of the Ozone Formation Potential from Pesticides Solvents Using a Mobile Ozone Chamber Assay", Journal of ASTM International, Vol. 5, No. 7, 2008.
- 2) US EPA, "Measurement of Gaseous Emission Rates from Land Surfaces Using an Emission Isolation Flux Chamber- User's Guide," EPA 600/8-86-008 (NTIS PB86-223161), February 1986.
- 3) SCAQMD Rule 1133.2 Attachment A- Guidelines for the Development of Source Test Protocols for VOC and Ammonia Emissions from Co-Composting Operations, Adopted January 10, 2003. South Coast Air Quality Management District.
- 3) Schmidt, CE, TR Card, "Validation of the Modified USEPA Flux Chamber Technology for Assessing High Advective Flow Sources such as Biofilters at Compost Sites," Paper # A446.2, Proceedings of the 101<sup>th</sup> Annual Meeting of the Air and Waste Management Association, Portland, Oregon, June, 2008.