



Minnesota
Pollution
Control
Agency

ENVIRONMENTAL BULLETIN

Volatile Organic Compound Emissions from Dry Mill Ethanol Production

by Daniel Brady and Gregory C. Pratt, Ph.D.

August 2006
Number 8

Abstract—Ethanol fuel production is a rapidly growing industry in the rural Midwest and is becoming a powerful economic and political force. With this rapid growth has come scrutiny of the environmental impacts of the industry. In 2002, the U.S. Environmental Protection Agency (EPA) and the Minnesota Pollution Control Agency (MPCA) entered into enforcement actions with 12 ethanol plants in Minnesota. The consent decrees that were ultimately negotiated revealed underreported emissions and required pollution control equipment to be installed in an effort to accurately quantify and reduce air emissions from ethanol plants. This effort also required stack testing that presented a number of challenges including developing testing protocols, quantifying and characterizing volatile organic compound emissions, and generating and analyzing data that could ultimately be used to assess health risks and inform regulatory action.

This case study chronicles Minnesota's experience applying air quality regulations to ethanol plants. A key component in this process was the collection of volatile organic chemical emissions data which were used to develop permit limits, gauge compliance and estimate risks. The database is relatively small, with several values below detection limits. In addition, emissions from some facilities are systematically different from others. These characteristics complicate the analysis of the data. To account for these issues a nested bootstrap procedure on the Kaplan-Meier method was used to calculate means and upper confident limits. The bootstrapping was done first over facilities and then over measurements within facility for 1000 repetitions of the Kaplan-Meier mean, taking the 50th percentile value as the mean, and the 95th percentile value as the upper confidence limit. The estimates of the 95% upper confidence limit of the mean may be used in risk analysis.

Introduction

Ethanol production in Minnesota was commercialized around 1990 with 11 million gallons produced in the state that year. In 2004, Minnesota generated approximately 400 million gallons from 14 plants that employed hundreds of people (Minnesota Department of Agriculture, 2005). There are presently three more plants under construction and two of the existing facilities are planning to expand to produce 100 million gallons individually each year. In a short period of time, fuel ethanol has become a booming business in Minnesota.

In October of 2002, 12 Minnesota ethanol plants entered into consent decrees with the EPA, MPCA, and the U.S. Department of Justice for violations of the Clean Air Act Prevention of Significant Deterioration (PSD) regulations as a result of underestimating emissions. The consent

decrees required each facility to pay a monetary penalty and to install best available control technology (BACT) to control nitrogen oxides (NO_x), carbon monoxide (CO) and volatile organic compound (VOC) emissions. In addition, the plants were required to test their emission units upon installation of control equipment to demonstrate compliance with the established emission limits in the consent decrees. These requirements were intended to easily confirm that the facilities' emissions were properly controlled and quantified. However, due to a number of unforeseen complications with regard to quantifying VOC emissions, the testing requirements proved problematic.

The consent decrees developed for Minnesota ethanol production facilities represent a significant accomplishment in correcting a calculation and design error that

had resulted in underestimated and uncontrolled emissions from fuel ethanol plants. They also have helped to ensure that future facilities will be constructed with the appropriate control technologies, thereby preventing excess pollutants from being emitted into the atmosphere. Minnesota's ethanol industry experience also led to the development of stack testing methodologies and information gathering that has implications not only for the ethanol industry but also for other industrial processes that involve drying of organic materials. This innovative source sampling effort produced a baseline data set that is the first of its kind. The testing that was carried out under these consent decrees provides a basis for permit conditions and for state VOC stack testing policy pursuant to those permit conditions.

The industry is expected to continue to grow in rural Minnesota as new plants are constructed to capitalize on tax incentives and a supportive political climate. The influx of facilities requires that regulators devote additional resources to permitting and related activities such as risk analyses that inform the permitting process. Perhaps one of the most useful products of the consent decrees is the generation of information that can be shared with all stakeholders, including regulators in other states. By initiating transparent processes and sharing information, regulators can fulfill their role of preventing unsafe levels of pollutants from being emitted during a time of enormous growth by this industry.

Fuel Ethanol Production Process

All of the 12 plants named in the Minnesota consent decrees were dry mill plants meaning that they dry the distilled grains, prior to shipping them as animal feed. Figure 1 shows the location of the ethanol plants subject to the consent decrees. Dry mill facilities account for about 55% of all fuel ethanol produced in the United States (Yacobucci and Womach, 2004). In this process, grain corn is initially run through a hammer mill and placed into a fermentation tank where enzyme additions and fermentation chemistry begins to convert the grain-water mixture into ethanol. After a series of fermentation tanks, the ethanol-containing mash is processed by distillation and molecular sieves into the final fuel product. The wet grain is removed from the fuel ethanol, sent to a rotary drum dryer and then sold as animal feed. The rotary drum dryer, which was typically vented to the outdoors, is the primary emission source on which BACT was required to control VOCs under the consent decrees. BACT has typically been determined to be some configuration of a thermal oxidizer that combusts the organic compounds in the effluent stream. Figure 2 shows a schematic of the dry mill ethanol process.

Figure 1: Location of Fuel Ethanol Plants in Case Study.

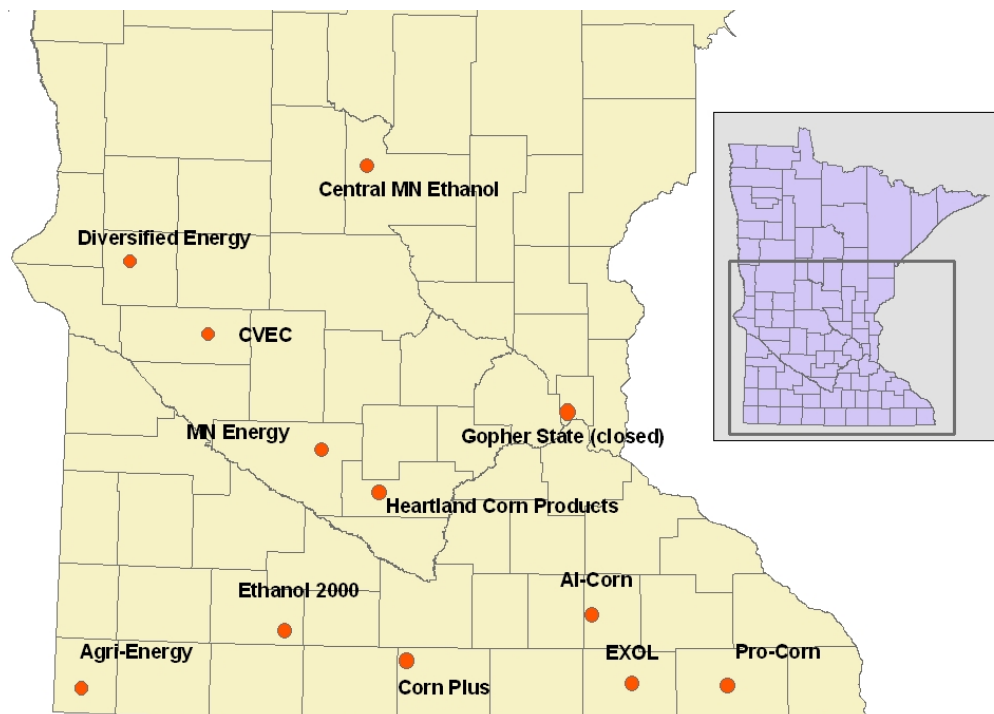
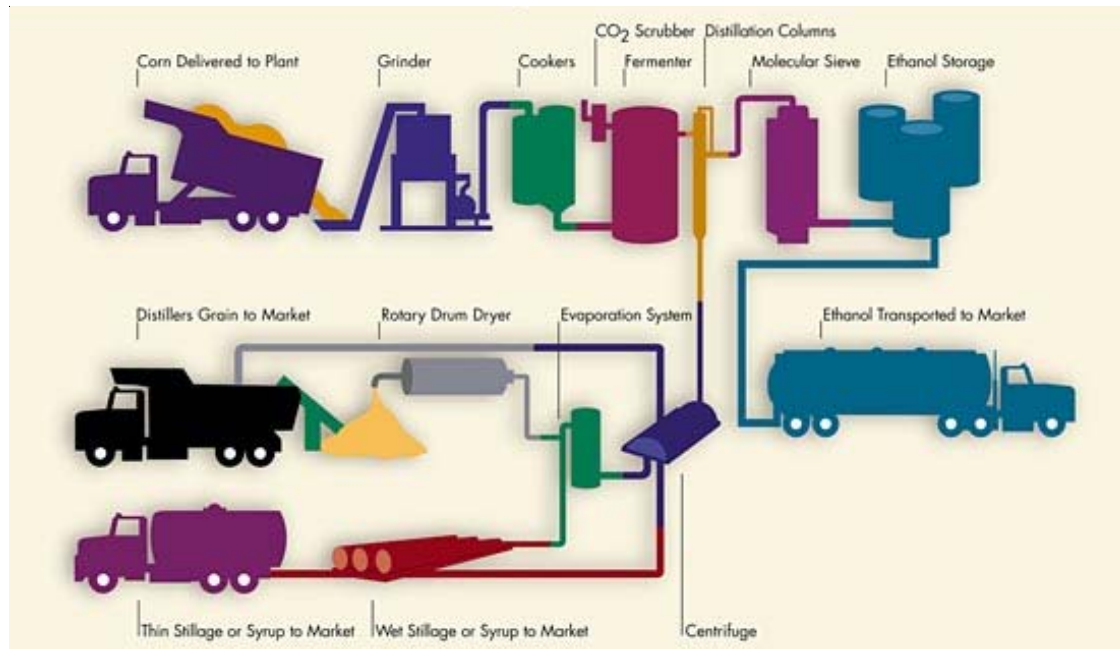


Figure 2: Schematic of the Dry Mill Ethanol Production Process.

Source: Renewable Fuels Association

All of Minnesota's ethanol facilities currently in operation fire natural gas to run their process and control equipment with propane often used as a back-up fuel. One plant under construction and another proposed facility will burn coal as a primary fuel source. The major sources of NO_x emissions from dry mill plants are the boilers used for facility operations, the dryer, and the control equipment ultimately placed on the dryers. In almost every case, this control equipment was a thermal oxidizer (TO) or a regenerative thermal oxidizer (RTO). Both are referred to here as simply thermal oxidizers (TOs). VOCs proved more elusive coming from multiple units at the plants including the dryer, distillation columns, fermentation tanks and scrubbers associated with these sources.

Quantifying VOC Emissions

Both regulators and the fuel ethanol industry agree that there are at least 8 to 10 VOC species that can be quantified from the gas stream of ethanol plant emission units. These species include acrolein, acetaldehyde, ethanol, furfuraldehyde, formaldehyde, acetic acid, lactic acid, and formic acid with some substitutions to this list at specific plants (EPA, 2004). EPA estimates that this list comprises approximately 60 to 90 percent of the gas stream while industry representatives maintain that these constituents account for 90 percent or more of the gas stream. There is little quantitative evidence to substantiate either position.

The effluent gas from ethanol plants can have a moisture content as high as 50 percent. The in-stack gas contains a large volume of moisture droplets that entrain organic chemicals and act like particles in the gas stream. Conventional stack testing for total VOCs (EPA method 25A) relies on instruments that draw gas through sampling equipment at a constant rate. The moisture in the gas is removed and the sample then passes through a flame ionization detector where volatiles are ignited and radiative

energy at specific wavelengths is recorded. Because the equipment used in this method does not adjust for isokinetic sampling (modifying the sampling rate to match the uneven flow across the stack diameter) as is generally done for particulate testing, the method is likely to underquantify any VOC that may be contained in the water droplets.

VOC testing currently accepted under method 25A is designed to report total VOC as “carbon” meaning it assigns a mass to the sample based on the amount of carbon present. It does not account for unevenly distributed species and larger oxygenated molecules. For example, in a gas stream where ethanol ($\text{CH}_3\text{CH}_2\text{OH}$) contributes more to the total mass than acetaldehyde (CH_3CHO , i.e., both having two carbon atoms), this test method would be unable to differentiate between the two and therefore fail to accurately characterize VOC emissions.

The chemicals listed earlier were only a starting point, and subsequent testing has indicated the presence of other species in the gas streams at most plants. Many compounds have been reported as “non-detect” values or “below detection limit” because the equipment used to sample the gas stream was not sensitive enough to quantify the actual amount present in the gas stream. This does not necessarily mean that the chemical is not present but rather that the chemical is likely present in some quantity between zero and the detection limit. Since there are possibly many compounds present below detection limits, the total VOC emissions represented by the sum of these unquantified emissions could be significant.

EPA attempted to resolve some of the measurement uncertainties by developing a testing protocol specifically for ethanol plants. This procedure, entitled the “Midwest Scaling Protocol,” employed a combination of existing testing methods. Since the major obstacle to traditional VOC testing was the entrainment of organic chemicals in water droplets, the solution was to sample the stack gases as if the source were emitting a particulate gas stream. This method required isokinetic testing and collection of samples in glass impingers, some containing sodium bisulfite solutions in order to precipitate out individual chemicals (EPA, 2004).

A “scaling factor” was developed to increase the total mass emissions quantified under Method 25A in order to account for the mass of chemicals not measurable. This factor was calculated from the speciated VOC data and applied to the total organic carbon mass measured by Method 25A which was performed in conjunction with the methodology as implemented by the Midwest Scaling Protocol. EPA developed a default scaling factor of 2.2 that could be applied to total VOC results from Method 25A in lieu of conducting speciated testing. In other words, the total VOC would be increased by a factor of more than two to account for the portion of chemicals not measured by the stack test but still contributing to the total mass of VOC. This scaling factor was designed to be “conservative,” that is, designed so that any error would be on the side of overestimating emissions.

Table 1 presents the averaged results from these tests between December 2002 and August 2004. For all facilities, these tests were performed after control equipment was installed as required by the consent decree. All tests were conducted by an independent testing consultant. Pre-test meetings were held with facility personnel, testing consultants, and MPCA staff to ensure that the test would comply with the combined methodologies described above. These meetings also served to discuss how the data would be reported (speciated, total mass, etc.). MPCA staff witnessed parts of most tests. Prior to submittal to the MPCA, reports were sent to the ethanol facility’s management or consultants for review and approval. Reports were then reviewed by the MPCA for accuracy, compliance with approved test methodologies, calibration of equipment, any problematic occurrences in the field, and chain of custody sample handling parameters, and ultimate verification of results.

Data Summary and Interpretation

Summary statistics for the ethanol plant emissions test data are presented in Table 1. Figure 3 is a graphical representation of the distribution of emission rates for each chemical from each type of emission unit. In general, most facilities consistently reported detectable levels of acetaldehyde, acetic acid, ethyl acetate, formaldehyde, ethanol and methanol at one or more emissions units. The amount of each species and that which is the predominant constituent varies across sources. Acetic acid and ethanol were the predominant emissions from cooling cyclones. From the single fluid bed cooler tested, acetic acid was the dominant emission. Acetaldehyde and acetic acid accounted for most of the emissions from thermal oxidizers. Fermentation scrubbers had the most diverse and highest overall emissions with significant amounts of acetaldehyde, acetic acid, ethanol, ethyl acetate, and isoamyl alcohol. Emissions of all substances were low from distillation scrubbers.

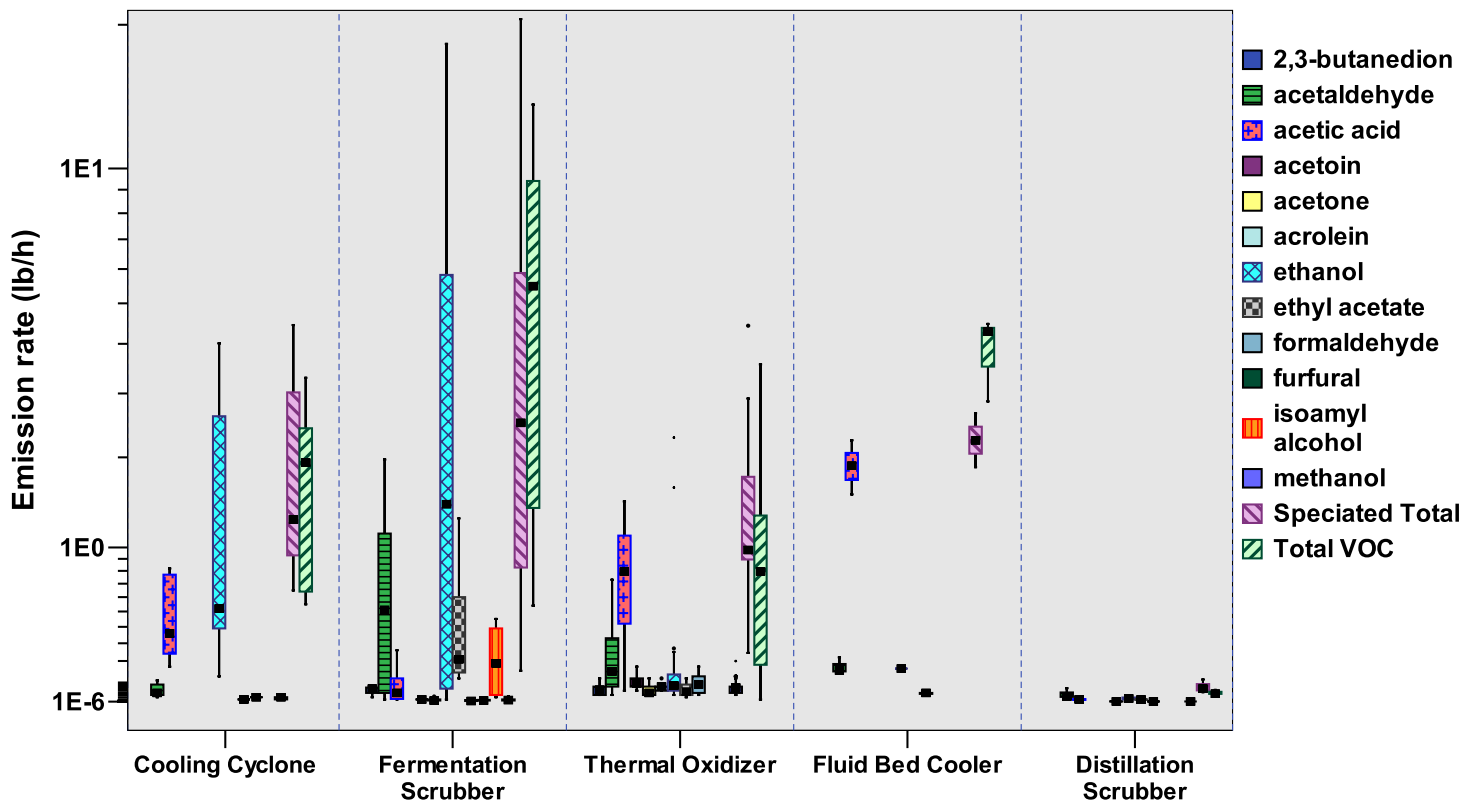
Several limitations in the data should be stated clearly. First, not all emissions units were tested for the same analytes, confounding comparisons among units and facilities. There is also considerable variation in the quantities of analytes across facilities, which we believe represents actual differences among facilities. The data are also left-censored, including values reported as zero and values reported as below detection limits. The proper treatment of values reported as zero or below detection is a matter of discussion. Ignoring such values will bias the data and lead to incorrect estimates of emissions.

In some cases the total speciated emissions (Method 18) did not match well with the total VOC measurement (Method 25A). The discrepancies were greatest for the thermal oxidizer test results at the Agri-Energy and Al-Corn facilities, along with one of the test runs at the EXOL facility. For these tests, the speciated VOC emissions were much larger than the total VOC measurement, a finding that appeared to be due to suspiciously low total VOC measurements and perhaps a better accounting of larger oxygenated compounds

Table 1: Summary Statistics of VOC Measurements at Ethanol Production Facilities. Units are Pounds per Hour (lb/hr).

Emission Unit	Statistic	2,3-		acetic acid	acetoin	acetone	acrolein	ethanol	ethyl acetate	formaldehyde	furfural	isoamyl alcohol	methanol	total speciated	total VOCs	percent speciated
		acetaldehyde	butanedion													
Cooling Cyclone	n	9		9				9		9		6	9	9	9	9
	n<dl	0		0				0		3		3	6	0	0	0
	min	0.02		0.17				0.12		<0.01		<0.02	<0.01	0.65	0.55	54%
	max	0.10		0.82				4.01		0.01		0.03	0.03	4.44	3.29	145%
	mean	0.05		0.44				1.28		0.01		0.02	0.02	1.83	1.78	105%
	95% UCL	0.08		0.65				2.48		NA		0.03	0.03	2.94	2.4	127%
Distillation Scrubber	n	3		3				3		3			3	3	3	3
	n<dl	0		0				1		0		0	0	0	0	0
	min	0.02		0.01			0.00	0.01	0.01	0.00a			0.00a	0.04	0.03	120%
	max	0.06		0.01			<0.0005	0.02	0.01	0.00a			0.00a	0.1	0.05	194%
	mean	0.04		0.01			NA	0.01	0.01	NA			NA	0.07	0.04	163%
	95% UCL	NA		NA			NA	NA	NA	NA			NA	NA	NA	NA
Fermentation Scrubber	n	17	3	17	3		17	17	14	17	6	6	14	17	17	17
	n<dl	0	0	6	3		15	0	0	6	5	0	10	0	0	0
	min	0.01	0.02	<0.01	<0.01		<0.005	0.01	0.11	0.00a	<0.005	0.02	<0.005	0.15	0.54	15%
	max	1.97	0.07	0.26	<0.01		0.02	18.27	1.28	0.01	0.01	0.45	0.02	20.56	13.67	183%
	mean	0.66	0.05	0.08	NA		0.006	4.20	0.39	0.005	0.01	0.22	0.007	5.62	5.9	88%
	95% UCL	1.19	NA	0.14	NA		0.009	9.41	0.73	0.007	0.01	0.45	0.012	10.11	7.76	127%
Fluid Bed Cooler	n	3		3				3		3			3	3	3	3
	n<dl	0		0				0		0			0	0	0	0
	min	0.14		1.54				0.16		0.03			1.87	2.86	44%	
	max	0.22		2.24				0.16		0.04			2.66	4.47	93%	
	mean	0.17		1.89				0.16		0.04			2.26	3.87	62%	
	95% UCL	NA		NA				NA		NA			NA	NA	NA	NA
Thermal Oxidizer	n	18	6	18	6	6	15	18	12	18			18	18	18	18
	n<dl	6	3	3	3	3	13	9	7	6			12	0	0	0
	min	<0.03	<0.05	<0.05	<0.05	<0.05	<0.05	<0.03	<0.03	<0.03			<0.03	0.25	0.01	25%
	max	0.73	0.06	1.46	0.17	0.03	0.07	2.28	0.11	0.17			0.20	4.43	3.56	9900%
	mean	0.21	0.03	0.73	0.08	0.03	0.05	0.28	0.04	0.08			0.05	1.46	1.1	877%
	95% UCL	0.36	0.07	1.00	0.11	0.11	0.06	0.68	0.07	0.11			0.09	1.97	1.88	3352%

a - values reported as zero on test report

Figure 3: Bar Chart of Speciated VOC Emission Rates by Emissions Unit.

through speciated testing than provided in Method 25A alone. The total VOC measurements also appeared anomalously low at the one distillation scrubber tested at the Al-Corn facility. At other emission units and other facilities the two test methods were in better agreement, although the variance among the test results was large.

While this small data set is far from perfect, it is still the most extensive available that we're aware of. It is clear that further, systematic testing is necessary to thoroughly characterize the complex gas stream from these facilities. EPA estimates that this testing captures approximately 60 to 90 percent of the constituents based on testing at one facility in 2001 comparing Method 18 results as carbon to Method 25A results. The ethanol industry believes the true percentage captured to be at the higher end of that range. The available data are insufficient to strongly support either contention. The percentage quantified may not be important to the type of controls installed or how the facility routinely operates, but imprecision in the information complicates accurate health risk analysis of the emissions from these facilities.

Use of Data in Risk Analysis

The MPCA has developed some experience in permitting ethanol plants. Recently, newly proposed plants have been asked to perform a risk analysis prior to permitting. Evaluating potential health effects from a facility is something new to the permitting process for ethanol production facilities and, as such, presents challenges. VOCs are usually risk drivers at ethanol plants, so scarcity and imprecision in VOC emissions data complicates the Air Emission Risk Analysis (AERA) process. The MPCA uses the AERA tool to identify potentially unacceptable health risks at new and expanding facilities. For most ethanol production facilities, the chemicals that pose the greatest risk are NO_x, acetaldehyde, formaldehyde, and acrolein. With the exception of NO_x, which can usually be well controlled and characterized, these chemicals are part of the complex VOC gas stream emitted by the plants.

In order to quantify potential risk, the analysis requires both reliable emission data and chemical-specific toxicity values that can be applied to the emission data. As discussed, VOC emissions at fuel ethanol production facilities

are not yet completely characterized. In addition, many of the measurable VOC species lack toxicity values and, therefore, can not be included in the quantitative assessment. In response to concerns over the lack of health benchmarks or toxicity values, the Minnesota Department of Health in 2005 developed interim benchmarks specific to chemicals emitted from ethanol plants. Even with the application of these values, however, only slightly more than half of the volatile organic compounds can be assessed quantitatively. The exposure durations indicated as problematic for an ethanol plant by the AERA are acute (one hour) and chronic cancer/non-cancer (evaluated based upon one year average concentrations). Generally, the chemicals from natural gas-fired ethanol plants are of concern to human health for short periods of exposure. However, we cannot say with complete certainty whether the data gaps have implications for risk analysis.

There is considerable toxicological information about a few of the ethanol plant emissions such as acetaldehyde and acrolein, and the respiratory impairments often attributed to NOx are well known. However, toxicity information about most of the rest of the identified emissions is less certain. Other chemicals yet unidentified could possibly increase the risk in one of the exposure scenarios (acute, chronic, subchronic or cancer, including multipathway). The data and the level of confidence in that data required for successful permitting is not necessarily adequate for a thorough human health risk assessment. The initial data collection was driven by the consent decrees, but that mandate does not require risk analysis at these facilities.

For purposes of cancer and chronic non-cancer risk assessment, EPA guidance recommends using the 95 percent upper confidence limit (95% UCL) of the arithmetic mean of stack test data: “The 95% UCL of a mean is defined as a value that, when calculated repeatedly for randomly drawn subsets of site data, equals or exceeds the true mean 95 percent of the time. The 95% UCL provides a conservative estimate of the average concentration. Due to the uncertainty associated with estimating the true average emission rate, the 95 percent UCL of the arithmetic mean should be used because it provides reasonable confidence that the true average emission rate will not be underestimated.” The EPA guidance does not address data sets with left censored (below detection) data.

The ethanol plant VOC emissions data contain many instances of left censored values. These were reported as less than a detection limit value or in a few cases as zero. In addition, it is clear from the data that emissions from some facilities are systematically different from others. To account for facility effects and for censored data a nested bootstrap procedure on the Kaplan-Meier method was used to calculate means and UCLs. The Kaplan-Meier method, also known as a product-limit estimate, is an estimator of the survival curve that does not assume any particular parametric family. It can be applied with flipping to treat left censored data. The bootstrapping was done first over facilities and then over measurements within facility for 1000 repetitions of the Kaplan-Meier mean. The 50th percentile value of the bootstrap Kaplan-Meier means was taken as the mean, and the 95th percentile value was taken as the UCL (Table 1). These 95% UCL values are suitable for use in a risk analysis.

Figure 4: Aerial View of a Typical Ethanol Facility.



References

- Armstrong, S. 1999. Ethanol: Brief Report on its Use in Gasoline. Cambridge Environmental, Inc. sponsored by the Renewable Fuels Association. Cambridge, MA.
- Interpoll Laboratories, Inc. 2003. Results of the December 4-5, 2002 Air Emission Compliance Test at the Ethanol 2000 Facility Located in Bingham Lake, Minnesota. Circle Pines, Minnesota.
- Interpoll Laboratories, Inc. 2003. Results of the January 28-30, 2003 Air Emission Compliance Test at the Agri Energy Facility Located in Luverne, Minnesota. Circle Pines, Minnesota.
- Interpoll Laboratories, Inc. 2003. Results of the January 21-23, 2003 Air Emission Compliance Test at the Al-Corn Clean Fuel Facility Located in Claremont, Minnesota. Circle Pines, Minnesota.
- Interpoll Laboratories, Inc. 2003. Results of the August 3, 2004 Air Emission Compliance Test at the Al-Corn Clean Fuel Facility Located in Claremont, Minnesota. Circle Pines, Minnesota.
- Interpoll Laboratories, Inc. 2003. Results of the April 1-2, 2003 Air Emission Compliance Test at the Pro-Corn Facility Located in Preston, Minnesota. Circle Pines, Minnesota.
- Interpoll Laboratories, Inc. 2003. Results of the August 26-29, 2003 Air Emission Compliance Test at the EXOL [Agra Resources] Facility Located in Albert Lea, Minnesota. Circle Pines, Minnesota.
- Interpoll Laboratories, Inc. 2004. Results of the January 20-29, 2004 Air Emission Compliance Test at the Diversified Energy Company Facility Located in Morris, Minnesota. Circle Pines, Minnesota.
- Interpoll Laboratories, Inc. 2004. Results of the June 2-4, 2004 Air Emission Compliance Test at the Chippewa Valley Ethanol Company Facility Located in Benson, Minnesota. Circle Pines, Minnesota.
- Knapp, K., Stump F., Tejada, S. 1998. The Effect of Ethanol Fuel on Emissions of Vehicles over a Wide Range of Temperatures. Journal of the Air and Waste Management Association. Vol. 48, no. 1047-3289, pp. 646-653. 1.
- Minnesota Department of Agriculture. 2005. Ethanol Plants in Minnesota, available at www.mda.state.mn.us.
- Minnesota Department of Health. 2005. Ethanol Sector Specific Interim Exposure Values for Air, available at <http://www.health.state.mn.us/divs/eh/risk/guidance/essievs.html>
- Renewable Fuels Association. Ethanol Production Process, available at www.ethanolrfa.org/prod_process.html.
- U.S. Environmental Protection Agency. 2004. Midwest Scaling Protocol for the Measurement of "VOC Mass Emissions" VOC Sampling at Wet and Dry Grain Mills and Ethanol Production Facilities. Office of Air Quality Planning and Standards.
- U.S. Environmental Protection Agency. 2000. Federal Reference Method 5, Particulate Gas Stream Sampling. Emission Measurement Center.
- USEPA, OSWER, 2002) Calculating Upper Confidence Limits for Exposure Point Concentrations at Hazardous Waste Sites (<http://www.hanford.gov/dqo/training/ucl.pdf>).
- Yacobucci, B., Womach, J. 2004. Fuel Ethanol: Background and Public Policy Issues. Congressional Research Service Report for Congress.

The MPCA's Environmental Bulletin Series is designed to highlight environmental outcomes and results of scientific studies the MPCA conducts in air, water and waste management. The bulletin is available electronically on the MPCA's web site at: <http://www.pca.state.mn.us>.

Correspondence with the author about this bulletin can be directed to Daniel Brady at daniel.brady@pca.state.mn.us or (651) 282-6144 or Gregory Pratt at gregory.pratt@pca.state.mn.us or (651) 296-7664. For more information about the Environmental Bulletin Series, contact either of the following MPCA staff of the Environmental Information and Reporting Unit.

Patricia Engelking (651) 297-3847
Tom Clark (651) 296-8580

Printed on recycled paper with at least 30 percent post-consumer waste.