⊕EPA

Project Summary

Evaluation of VOC Emissions from Wastewater Systems (Secondary Emissions)

R.D. Cox, J.I. Steinmetz, D.L. Lewis, and R.G. Wetherold

This study was performed to develop and evaluate procedures for measuring or estimating VOC emissions from wastewater treatment facilities. The report describes the results of field sampling at two wastewater treatment facilities and a comparison of measured VOC emissions with emissions data obtained through predictive modeling. One of the facilities tested used aerobic biological treatment, whereas the second used anaerobic treatment. The field measurement techniques and equipment, laboratory measurement techniques, data reduction, and the predictive model are described. Also, a thorough quality control/quality assurance program that documents the data quality is described. The results of this study provide information on the errors to be expected when using predictive models to estimate VOC emissions from wastewater treatment facilities as well as when measuring VOC emissions using the Concentration-Profile technique.

This Project Summary was developed by EPA's Industrial Environmental Research Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

Few data are available concerning quantitative definition of VOC emissions during treatment of chemically contaminated wastewaters. In general, wastewater treatment systems are evaluated only with respect to concentrations of pollutants in the water effluent. Emissions of pollutants to the atmosphere are usually ignored or even considered a means of increasing water treatment efficiency. To properly evaluate VOC emissions during wastewater treatment requires accurate techniques for identifying and quantitating emissions, as well as a good understanding of the volatilization and dispersion processes.

The quantitation of VOC emissions from water basins requires consideration of two processes: emission and dispersion. Surface emission measurements can be divided into direct and indirect. Direct measurements involve only measuring emission processes directly over the water surface. Indirect measurements involve determining VOC concentrations in the air above the surface or downwind of the basin and using micrometeorological dispersion modeling to relate measured concentrations to emission rates.

An understanding of the thermodynamic principles associated with emissions during wastewater treatment has led to the development of models for predicting VOC emissions. These models require significantly less testing than the testing required to actually quantitate emissions. These models generally only require inputs such as VOC concentrations in the water, ambient temperatures and wind speeds, engineering functions of the treatment facility, and thermodynamic properties of the compounds of interest. However, little information is available concerning the accuracy of predictive models when applied to real-world wastewater treatment conditions.

The technical objective of this study was to examine and refine a method for the indirect sampling of volatile organic carbon

(VOC) emissions from wastewater treatment facilities for the synthetic organic chemicals manufacturing industry (SOCMI), and to evaluate a predictive model using actual emissions data. The method that was refined and used to measure VOC emissions was the Concentration-Profile (C-P) technique. This procedure involved field determinations of temperature, wind speed, and time-averaged concentrations of VOC and specific compounds, all as a function of distance above the wastewater pond surface using a logarithmic interval design. VOC species and chemical class concentrations were measured at two sites using the C-P technique. These concentrations were compared to emissions obtained using predictive models. The sampling and predictive techniques were applied to two sites, one using subsurface aeration, and the second, an anaerobic treatment facility.

Approach

The approach of this study involved an evaluation of the sampling restrictions of the C-P technique and a modification of the sample collection and analysis portion of the technique. This was followed by screening of several sites by visits and limited testing, selection of two sites for extensive testing, and development of site-specific test plans and a quality assurance project plan. Field sampling was then performed at two sites, and results of the emissions measurements were compared to emission rates obtained from predictive modeling. A thorough quality assurance program and statistical treatment of experimental data allowed the establishment of confidence limits for the comparison of experimental and predictive results.

An evaluation of the C-P technique demonstrated that minimum requirements for the wastewater basin and atmospheric stability were necessary for proper application of the technique. The criteria used for proper sampling are:

- The location selected for C-P testing must be at least 50 (and preferably 200) times the distance of the height of the dike or other significant obstacle away from the edge of the pond along the direction of average wind. Profile measurements taken closer than this cannot reflect the log profile assumed in the methodology and, consequently, the emissions data will not be valid.
- The mean wind speed for the 20-minute sampling period must be greater than 5 mph.
- The maximum wind speed (gust) must not be greater than three times the mean wind speed.
- The wind direction standard deviation (WSD) must not be greater than 45°.

- The Richardson number (R_i), defining atmospheric stability, must be greater than -0.1.

As presented, the C-P technique called for collecting VOC species using liquid oxygen traps for field sampling. This method presented a number of safety and procedural problems and was therefore not used. Instead, air samples were collected in evacuated stainless steel canisters using vacuum flow regulators to obtain integrated samples. Extreme care had to be used to minimize contamination with this technique. Different types of canisters were found to have significantly different blank levels. The canister technique proved to be a simpler and more workable technique than liquid oxygen traps.

The determination of chemical flux rates above waste treatment ponds by the C-P technique required measurements of wind speed, temperature, and organic species concentrations at six logarithmically spaced heights over the pond surface. In addition, measurements of humidity, water temperature, and organic composition of the water were required. A 20-foot pontoon boat was outfitted with the necessary equipment to provide these measurements and with safety equipment for sampling personnel. The sampling equipment consisted of a 4-meter mast with six wind speed sensors, six temperature sensors and seven air collection probes, a continuous real-time data collection system, water temperature and sampling equipment, and an instrument for measuring humidity.

The work performed during this program incorporated a comprehensive quality assurance/quality control (QA/QC) program as an integral part of the overall sampling and analytical effort. The primary objective of the QA/QC program was to provide a system for defining the measurement data quality in terms of precision and accuracy. It also provided a mechanism for assuring that the data were representative, complete, and comparable to other similar data. While the system of QA activities was necessarily independent of the technical effort *per se,* the QC system was an integral part of the daily technical effort. It was designed to provide an overall system for generating data of a specified quality. The QA/QC program encompassed control over daily data generation as well as a mechanism to assess the quality of data produced. This ultimately allowed the establishment of confidence limits for comparing predictive and experimental data.

Results and Discussion

VOC emissions were measured using a modification of the C-P technique at two

chemical waste treatment facilities, one using an aerobic bio-oxidation pond (site FB), and the second using a non-aerated pond (site TB). Three sets of C-P tests were performed at each site. Also, water samples were collected for applying the predictive models. Due to an equipment malfunction, water samples from site FB were destroyed and a second set of samples was collected approximately one month after the C-P sampling. All quality control functions were performed at both sites and quality assurance audits were conducted at site TB and at Radian's laboratories.

Results of the C-P sampling and the predictive model applications are presented in Table 1. Emissions from both sites were very low, near the detection limits for the sampling and analytical methods which were used (3 ppbv-C). VOC flux rates were calculated for benzene, diethyl ether, indene, and styrene at site FB. Also, a flux rate was determined for the total aromatic content in the air above the pond surface. Measured flux rates at this site ranged from 430 kg/Ha-yr for styrene to 3660 kg/Ha-yr for diethyl ether. The average flux rate for total aromatics at this site was 20,400 kg/Ha-yr. VOC flux rates at site TB were determined for benzene, cyclohexane, and acetone. Measured flux rates at this site ranged from 130 kg/Ha-yr for benzene to 1550 kg/Ha-yr for acetone. Standard errors and confidence limits were calculated for all analytical and meteorological measurements. Because of the low levels of VOC species that were present above the ponds, and sampling and analytical variabilities, a zero flux rate was within the 95% confidence level for all flux measurements.

Flux rates determined using the modified C-P technique were compared to flux rates from the predictive models. Results of the comparison, shown in Table 1, were variable and appeared to be related to the type of compound and whether or not aerators were used. For the site containing aerators (FB), predictive flux rates for the three aromatic compounds were approximately 3.5 times higher than measured flux rates. However, for diethyl ether, the predicted flux rate was only 35% of the measured flux rate. Predicted flux rates for diethyl ether and styrene were within the 95% confidence limits for the measured rates, whereas benzene and styrene were outside the 95% confidence limits. The predictive model indicated that 85-95% of the overall emissions at site FB resulted from aeration (turbulent phase).

For the site not containing aerators (TB), predictive flux rates for benzene and cyclohexane were greater than measured rates by factors of 10.0 and 5.9, respectively. The predicted flux rate for acetone at this site was

15% of the measured rate. The predicted flux rate for acetone was within the 95% confidence limits for the measured value, but predicted flux rates for benzene and cyclohexane were not.

In summary, predicted flux rates range from 0.15 to 10 times the measured flux rates at two sites. Predicted rates for aliphatic and aromatic hydrocarbons were always higher than measured rates, whereas predicted rates for the two polar species, diethyl ether and acetone, were lower than the measured rates. The lower predicted flux rates for the polar compounds may be attributed to low analytical data on these compounds in water, since these do not purge efficiently using routine purge and trap techniques. Data from site FB should also be viewed in light of the fact that VOC species concentrations in the water (used for predictive modeling) were not obtained on the same day as air flux rate data.

Results of the QA/QC portion of this project indicated that the overall chemical data accuracy was -12%, and the combined sampling and analytical precision (variability) for ambient species measurements was ±34%. The data accuracy must be viewed in light of the fact that primary standard reference materials are not available for ppb levels of organic vapors in air.

Conclusions and Recommendations

The C-P technique used to measure flux rates is an indirect measurement technique, since it requires micrometeorological modeling to convert measured concentrations to flux rates. Validation of the predictive model should only be considered a relative comparison between the predictive model and the micrometeorological model used for measuring flux rates. In the future, it is recommended that both models be com-

pared to emission rates determined by a direct measurement technique.

The meteorological and height-to-berm requirements of the C-P technique seriously limit its applicability on smaller ponds. Some treatment facilities use small settling and cooling ponds before larger scale treatment. Both systems tested had initial settling ponds. Because of elevated temperatures and concentrations in these ponds, they can potentially produce significant emissions. A measurement technique should be developed and evaluated for smaller ponds.

Table 1.   Comparison of Predicted and Measured Flux Rates

Species or Class	Predicted Flux		Average Measured Flux[a]		Predicted	Measured Flux Confidence Limits (95%)[b]		Predictive Flux Within Limits?
	ng-C/cm²-sec	kg/hectare-yr	ng-C/cm²-sec	kg/hectare-yr	Measured	ng-C/cm²-sec	kg/hectare-yr	
Site = FB								
Benzene	0.208	7,150	0.0592 ± 0.0492	2030 ± 1680	3.5	0 - 0.158	0 - 5390	No
Diethyl Ether	0.0266	1,300	0.0751 ± 0.0561	3660 ± 2730	0.35	0 - 0.187	0 - 9120	Yes
Indene	0.0889	3,010	0.0261 ± 0.0167	880 ± 570	3.4	0 - 0.0595	0 - 2020	No
Styrene	0.0438	1,500	0.0126 ± 0.0261	430 ± 890	3.5	0 - 0.0647	0 - 2210	Yes
Total Aromatics	0.586	20,400	0.120 ± 0.0829	4180 ± 2890	4.8	0 - 0.286	0 - 9960	No
Site = TB								
Benzene	0.0394	1,340	0.0038 ± 0.0138	130 ± 480	10.0	0 - 0.0313	0 - 1090	No
Cyclohexane	0.0381	1,400	0.0065 ± 0.0134	230 ± 490	5.9	0 - 0.0333	0 - 1210	No
Acetone	0.00458	240	0.0313 ± 0.0168	1550 ± 860	0.15	0 - 0.0650	0 - 3270	Yes

[a] Mean ± standard error (σ).
[b] Mean ± 2σ.

United States
Environmental Protection
Agency

Center for Environmental Research
Information
Cincinnati OH 45268
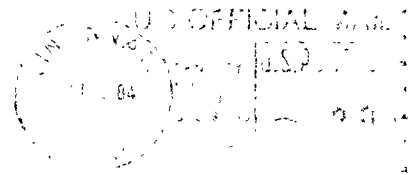
Official Business
Penalty for Private Use $300