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Project Summary

Field Assessment of Air Emissions and Their Control at a Refinery Land Treatment Facility

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A field assessment was performed to measure the emissions of volatile organics from a petroleum refinery land treatment site. As part of this study, the emissions of total volatile organics from surface-applied and subsurface-injected oily sludge were measured over a five-week period. The effect of soil tilling on the emissions was also monitored.

Volatile organic emission rates were measured using the emission isolation flux chamber method. Emission rates of carbon dioxide and methane were also measured for use in evaluating and estimating apparent biodegradation rates. Soil samples were collected during the test periods to determine soil properties, oil levels and microbe count. Soil surface and ambient temperatures inside the flux chambers were also measured throughout the test periods to determine their influence on emission rates.

From the measurements, the emission rates of total volatile organics, as well as the emission rates of selected individual volatile organic species, were estimated over the five-week period. The amount of oil biodegradation was estimated from carbon dioxide evolution rates and oil disappearance from soil samples over the test period. The measured volatile organics emission rates and the emission rates of selected species were compared to the rates predicted with The Thibodeaux-Hwang land treatment model.

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

Introduction

The Office of Air Quality Planning and Standards (OAQPS) of the U.S. Environmental Protection Agency (EPA) is developing standards for controlling emissions from hazardous waste treatment, storage and disposal facilities (TSDFs). The purpose of these regulations is to protect human health and the environment from impairment by emission of volatile organic compounds (VOCs*) and particulate matter. The Hazardous Waste Engineering Research Laboratory (HWERL) has the responsibility of providing technical support to OAQPS in the area of atmospheric emissions determination from hazardous waste management. Part of the research in the HWERL program involves the study and assessment of emission control techniques which are applicable to TSDFs.

In the current study, the emission characteristics of the land treatment of oily sludges by surface application and subsurface injection techniques were evaluated. The results of this assessment have increased the understanding of volatile organics emissions from land treatment disposal facilities. The subsur-

*VOCs are defined in this study as those purgeable volatile compounds determined by a purge-and-trap technique.

face injection technique was selected for this study because the technique is believed to represent a potentially major type of volatile organics emission control at TSDFs.

To assess the effectiveness of subsurface waste injection as an emission control technique, a field study was performed at the land treatment facility located at the Chevron, USA refinery in El Segundo, California. The major objectives of the study at this site include the following:

- To determine the percentage of volatilized organics as a function of the applied purgeabale organics and of the applied oil;
- To estimate the emissions of applied volatile organics from the test plots for the five-week testing period and annually for the entire land treatment facility;
- To determine the effectiveness of subsurface injection in reducing volatile organic emissions from land treatments by comparing the measured emission rates from the two application methods;
- To determine the extent of oil degradation and/or measurable biological activity;
- To determine the effects of various environmental and operational parameters on emission rates and emission rate measurements, including those due to the emission measurement procedure; and
- To compare the measured emission rates to those calculated using the Thibodeaux-Hwang predictive emission model.

Approach

The land treatment area at the Chevron, El Segundo refinery covers approximately 42,000 square meters (10 acres). Three test plots, each approximately 420 square meters (0.1 acre) in area, were located side-by-side at one corner of the facility. The area containing the test plot has been in land treatment service for several years.

Experimental Design—The test design was a synthesis of two sampling strategies for obtaining emission measurements: totally randomized sampling over the test plots and semi-continuous sampling at a single location in each plot. Three test plots were used in this study. Sludge was surface-applied to one plot (Plot A) and subsurface-injected on another plot (Plot C). In between these two plots was a third plot (Plot B), and no sludge was applied to this plot during the test period. Plot B served as a baseline or control plot. Each plot was divided into 21 equal segments to provide for randomized sampling.

Sampling was performed during the first, third and fifth weeks of a five-week period. Samples were collected in the morning and afternoon. On two days, samples were collected immediately before dawn so that nighttime emissions could be estimated.

Sampling Procedures—The main sampling technique employed at this site involved the direct measurement of emissions using the emission isolation flux chamber. A diagram of the flux chamber is shown in Figure 1. The flux chamber is placed on the emitting surface. Clean, dry air is passed through the chamber at a controlled and measured rate. The concentration of the specie(s) of interest is measured at the outlet of the chamber. The emission rate of the measured species(s) from the enclosed surface can then be calculated from the flow rate and concentration in the gas.

Liquid grab samples of the sludge and the service water used to irrigate the soil were collected. Samples of soil were also collected periodically during the testing. Type K thermocouples were used to monitor the air and soil temperatures both inside and outside of each flux chamber.

Analytical Procedures—The on-site analyses were limited to gas-phase analyses of the air samples collected in gas-tight syringes from the outlet of the flux chambers. A Byron Instruments Model 401 total Hydrocarbon (THC) analyzer was used to determine the concentrations of total hydrocarbons (THC), CO_2 and methane in the effluent air samples from the flux chamber.

The off-site analyses included the chemical speciation of the flux chamber air samples collected in stainless steel canisters and of the liquid sludge and water samples collected at the land treatment site. The oil, moisture, and microbe levels in the soil were also determined, as were the physical properties of the soil samples.

The oil, water and solids content of the sludge samples were determined by a method developed for this purpose by Chevron Research Corporation. This method is called the Modified Oven Drying Technique (MODT). The oil and grease content of the soil samples was determined by EPA Method 413.1. Standard methods were used to determine the bulk density, particle density, total porosity, moisture content and particle size distribution of the soil samples.

Sludge Application—The sludge was applied as evenly as possible to the

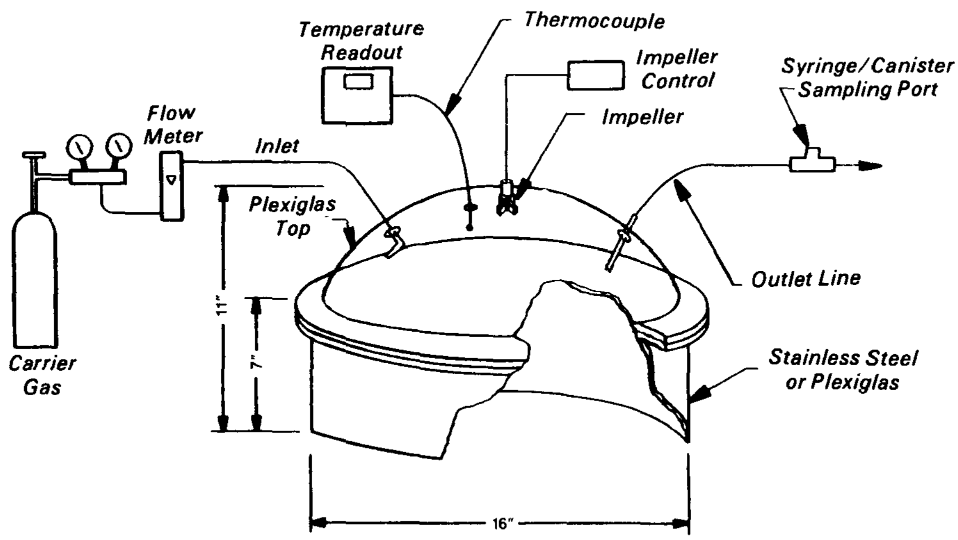

Figure 1. *Cutaway side view of emission isolation flux chamber and sampaling apparatus.*

urface-applied Plot A and to the subsurface-injected Plot C. The sludge was injected subsurface using an 8000 liter (50-barrel) capacity injector vehicle equipped with four separate injector tines. The waste was injected 15-28 cm (6-11 inches) below the surface. The average waste loading was 1.4 x 10^4 kg/plot, assuming equal application rates for both plots. All three plots were tilled with a disk tiller pulled behind the tractor during the sludge application.

Emission sampling with the flux chambers was started immediately after application and continued for four days. Emission sampling was performed during two other four-day periods in the third and fifth weeks following application. Each plot was tilled 2-3 times per week during the five-week test period. The plots were also irrigated with water once between the first and second sampling periods and three times between the second and third sampling periods.

Emission Estimates—Based on the emission measurements performed in this study, total-VOC emissions were estimated for the individual test plots for a five-week period. To do this, nighttime emissions were estimated by interpolating between late afternoon and early morning measurements. Daily emissions for days on which no measurements were taken were determined by interpolating between days when emissions were measured.

Annual emissions were also estimated for the whole facility so that emissions reductions potential for emissions controls could be determined. To estimate annual emissions, five week test-plot emissions were extrapolated, to the whole facility by accounting for facility waste application rates, application methods and surface area.

Emission Modeling—Instantaneous emission rates were calculated using the Thibodeaux-Hwang model. Total-VOC emissions were calculated using average physical and chemical properties for various classes of volatile compounds (e.g., volatile aromatics), properties of the test plot soil and site-specific environmental parameters. Similarly, the emission rates of the 12 compounds studied individually were calculated based on their individual physical and chemical properties.

Results and Discussion

The following site-specific findings were obtained from this study.

Total Volatile Organic Emission Rates

The average emission rates for each plot over the five-week test period were 47.1, 6.16, and 53.9 $\mu g/m^2$-s of volatile organics for the surface applications (Plot A), background (Plot B), and subsurface application (Plot C) plots, respectively. The instantaneous emissions from each of the three plots were as high as 370.7, 38.5, and 324.9 $\mu g/m^2$-sec, respectively.

The emission rate decreased approximately exponentially with time after application for each plot. Comparing the averaged measured emission for the first week of sampling to the third and fifth (final) weeks of sampling, the emission rates decreased 93%, 86%, and 91% for the surface application, background, and the subsurface application plots, respectively. The weekly estimated emission rates are shown graphically in Figure 2. The five-week estimated cumulative emissions for Plots A, B, and C were 33.3, 5.2, and 39.0 kg, respectively.

It was estimated that the ratio of volatile organics emitted over five weeks to purgeable organics in the waste was 0.30 for Plot A and 0.36 for Plot C. The ratio of volatile organics emitted over five weeks to the mass of applied oil was estimated to be 0.012 for Plot A and 0.014 for Plot C.

The measured emission rates were found to be related to the ambient air temperatures above the soil surface. This resulted in a significant diurnal effect in emissions. For the two occasions when sampling was conducted before dawn, the average measured emission rate for the "half-day" (i.e., four-hour) period was lower than the average of the half-day averages for that week for each plot. For Week 1, the decrease was 75%, 56%, and 87% for Plots A, B and C, respectively. For the second week of sampling, the decrease was 75%, 54% and 59% for Plots A, B and C, respectively.

Subsurface Injection as an Emissions Control Technique

The application method as practiced at this refinery did not appear to have a large effect on the emissions. Immediately after sludge application and before the first tilling, the cumulative measured emissions from the surface application plot were slightly greater than those from the subsurface application plot. After the first tilling episode (two days after the initial application), the cumulative measured emissions seemed to be slightly greater for the subsurface application plot throughout the remainder of the test period. The total cumulative measured emissions were

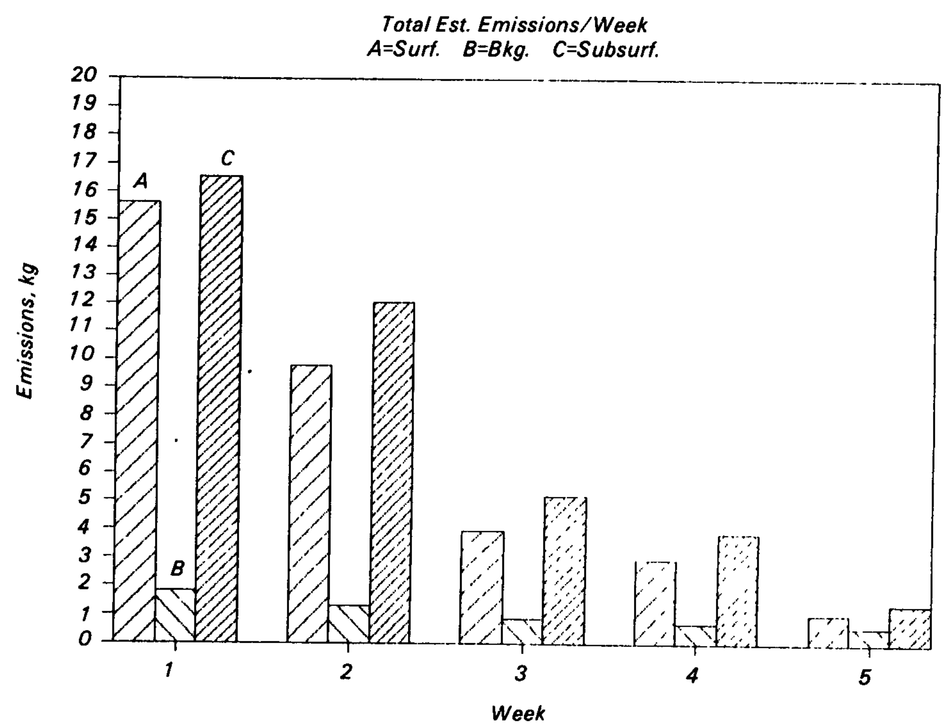

Figure 2. *Total weekly estimated emisisons for each plot.*

14% greater from Plot C than Plot A. Similarly, the estimated total emissions from Plot C (39.0 kg) were 17% greater than the total for Plot A (33.3 kg) for the five-week test period.

Because the difference between cumulative emission rates for Plots A and C were small and were comparable to the uncertainties in emissions rates themselves, it is not possible to draw conclusions regarding the relative emission characteristics of the two application plots. However, any difference did not appear to be significant.

Emissions of Individual Compounds

The emissions of 12 selected individual compounds consisting of alkanes, alkenes and aromatics were also studied in detail. The dozen individual compounds examined behaved in the same manner as the total volatile organics. The emissions rates decreased with time, increased after tilling, and showed diurnal fluctuations. However, the application method had a greater effect on the individual compounds than for total volatile organics. Also, a greater percentage of the applied individual compounds was emitted than for total volatile organics. The difference between the average emissions values and those of the 12 selected compounds is thought to be due to the differences in volatilities of the 12 selected compounds and the average volatility of the oily sludge.

Biodegradation and Oil Disappearance

Radian measurements indicated that little or no biodegradation of the applied oil was observed. No methane was detected, implying that no anaerobic degradation occurred. Significant quantities of possible products of partial degradation were not detected. Because of the scatter in the data, neither a change in microbial population levels nor a decrease in oil content in the soil could be discerned. The measured carbon dioxide (CO_2) values were at near background levels. Assuming all CO_2 measured was due to complete aerobic degradation, less than 3% of the applied oil was completely degraded over the five-week test period.

Chevron analyzed more soil samples using a recently developed analytical technique. One or both of these factors contribute to more precise measuremen of the variation of oil content with time The Chevron results appear to indicat a decrease in oil levels in the soi However, even these data show signif icant scatter; only one of the fou monitored sampling points exhibited change in oil content which had greate than a 95% certainty of being nonzero.

Emissions Model

The Thibodeaux-Hwang model for lan treatment facilities was found to predic mean emission rates that were generall higher than those actually observed, bu which agreed to within an order c magnitude. The model predicts an expo nential decay in emissions over tim which approximately agrees wit observed changes in emissions at th site.

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***Benjamin L. Blaney** is the EPA Project Officer (see below).*
The complete report consists of two volumes entitled "Field Assessment of Air Emissions and Their Control at a Refinery Land Treatment Facility:"
Volume I (Order No. PB 88-124540/AS; Cost: $32.95, subject to change).
Volume II (Order No. PB 88-124557/AS; Cost 32.95, subject to change).
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