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Project Summary

Laboratory Assessment of Potential Hydrocarbon Emissions from Land Treatment of Refinery Oily Sludges

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Volatile organic emissions were characterized when oily petroleum sludges from refineries were incorporated in soils under controlled laboratory conditions. The sludges tested included three of the five listed hazardous wastes for the refining industry: dissolved air flotation float, slop oil emulsion solids, and API separator sludge. The volatile components of the sludges were first identified. Then the effects of air temperature and humidity, wind speed, soil type, temperature and moisture, sludge loading and volatility, and method of waste application were studied. The volatile components identified in the sludge were also present in the emissions from the soil-waste mixtures. The quantity of emissions was most affected by the sludge volatility, sludge loading, application method, and atmospheric humidity; the cumulative emissions at a given period of time could be correlated with these operational variables. The emission rate or level was not significantly affected by soil type or soil moisture. An expression for estimating the rate of emissions as a function of elapsed time after application could not be developed from the data. Although every effort was made to simulate actual land treatment conditions, it was not possible to apply these laboratory findings directly to predict full-scale results.

This Project Summary was developed by EPA's Robert S. Kerr Environmental Research Laboratory, Ada, OK, 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). The research effort was jointly funded by the USEPA and the American Petroleum Institute.

Introduction

Land treatment has been used extensively by the petroleum refining industry to attenuate oily sludges, predominantly on company property. In the current process of renewing land treatment permits, there has been an increasing interest in addressing the characteristics and magnitude of volatile organic emissions occurring in land treatment operations.

This laboratory study was performed to assess the atmospheric emissions from the land treatment of refinery sludges, particularly those listed as hazardous wastes for petroleum refining in 40 CFR 261.32 and which are routinely land treated by the industry. The wastes studied were API separator sludge, slop oil emulsion solids, and dissolved air flotation (DAF) float. The magnitude and characteristics of the emissions and the variables affecting them were investigated using sludges and soils collected from participating refineries.

Procedures

The volatile organic constituents of the sludges were identified by using a purging device, trapping the emitted organics, and performing analyses by gas chromatography/mass spectrometry

(GC/MS). A laboratory land treatment simulator apparatus was constructed to measure air emissions from soil/waste mixtures while controlling and measuring air velocity, humidity, and temperature, and soil temperature and moisture. A series of tests was conducted with this simulator using eight soil samples and nine sludges obtained from eight participating refineries. Initially, nine variables were evaluated with the simulator (Table 1). Based on these preliminary studies, the five variables indicated by asterisks in Table 1 were chosen for further intensive study. Table 2 is the experimental matrix for evaluating these variables, where one variable was studied while holding the four others constant. The remaining variables in Table 1 were held constant: air and soil temperatures at 90°F, wind velocity 3 mph, and sludge application mode being to the surface. Emissions measurements consisted of total hydrocarbons as measured by a Byron Instruments 401 Total Hydrocarbon Analyzer and individual compound identification by collection in steel cylinders and dual detector GC analysis using normalized toluene response as the indicator of the compound present.[1]

Results and Discussion

The sludge characteristics are presented in Table 3 (nonspecific organic content) and in Table 4 (specific organic compounds identified). Fifty-two runs were made with the land treatment simulator. Statistical interpretation identified the parameters having the most significant affects on emission levels: sludge volatility, sludge loading, and air humidity. The emission rate or level is not significantly affected by type of soil or its moisture content. In general, the results showed that the more volatile components identified in the sludges are emitted to the air, specifically C_9 - C_{12} alkanes, xylenes, C_3-benzenes, toluene, and benzene. The more volatile compounds were present in the emissions at relatively higher concentrations compared to the concentrations in the sludges that were the respective sources of the emissions. The cumulative emissions at a given period in time (four to seven hours after application) can be correlated with sludge volatility, sludge loading, and atmospheric humidity. During the two phases of the study, the hydrocarbon volatilization ranges, expressed as % oil content in sludges applied, were 0 - 3.6% after 30 minutes and 0-6% after 4 hours applied. An expression for estimating rate of emissions as a function of elapsed time after sludge application could not be developed from the data obtained.

All of the specific organic compounds identified in the emissions from each of the runs is tabulated in the report together with the measured concentrations in parts per million by volume expressed as carbon (ppmv-C).

Table 1. *Operational Variables Studied with the Land Treatment Simulation Apparatus*

*Sludge Volatility	*Soil Type
Application Mode	*Soil Moisture
*Soil Loading	*Air Humidity
Air Temperature	Air Flow
Soil Temperature	

Table 2. *Experimental Matrix for Evaluating Operational Variables*

	Sludge ID	
Sludge Volatility:	Low	SL-12
	Medium	SL-13, SL-14
	High	SL-11
	Soil ID	
Soil Type:	D-1	Silty sand
	D-8	Silty clay
	D-7	Sandy Silt
Sludge Loadings:	5 levels (0.05 - 2.0 lb oil/ft^2 soil)	
Soil Moisture:	5 levels (5 - 25 wt. %)	
Air Relative Humidity:	3 levels (30 - 80%)	

Table 3. *Nonspecific Organic Composition of Sludges*

Sludge	Type	Oil & Grease (wt. %)	Volatilized hydrocarbons[a] (PPM/ml sludge)	Sum of volatilized compounds identified[b] (μg/gm)
SL-11	API Sludge	22	820	6,100
SL-12	DAF Float	1	70	760
SL-13	Slop Oil	2	125	2,910
SL-14	API Sludge	2	103	850

[a]*Average total hydrocarbon concentration in vapor phase over 4 hrs. nitrogen purging using 1 ml sludge (expressed as hexane).*
[b]*Total concentration of emitted compounds identified by GC/MS (see Table 4).*

Table 4. *Major Organic Compounds Identified in Sludges*

Compound	Sludges SL-11	SL-12 (μg/g)	SL-13	SL-14
Benzene	540	32	18	5
Toluene	1,700	58	98	14
M/P-Xylene	700	58	110	30
O-Xylene	330	28	50	16
C_3-Benzene	1,100	150	400	160
C_3-Benzene	890	120	400	140
Napthalene	230	34	350	64
Anthr./Phen.	150	20	1,100	92
C_9-H.C. (alkane)	130	30	14	36
C_{12}-H.C. (alkane)	140	57	210	120
C_{17}-H.C. (alkane)	84	72	84	68
C_{17}-H.C. (alkane) (pristane)	66	72	24	68
C_{19}-H.C.	31	26	40	28
C_{20}-H.C.	2	NM	16	14

References

[1]Cox, R.D. and R.D. Earp "Determination of Trace Level-Organics in Ambient Air

by High-Resolution Gas Chromatography with Simultaneous Photoionization and Flame Ionization Detection," Anal. Chem. *54* (13) 2266, November, 1982.

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The complete report, entitled "Laboratory Assessment of Potential Hydrocarbon Emissions from Land Treatment of Refinery Oily Sludges," (Order No. PB 84-209 766; Cost: $13.00, subject to change) will be available only from:
National Technical Information Service
5285 Port Royal Road
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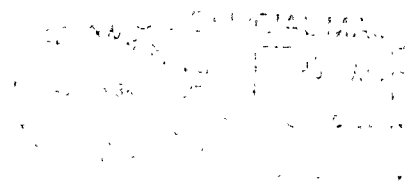

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