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Project Summary

Preliminary Assessment of Air Emissions from Aerated Waste Treatment Systems at TSDFs

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Aerated wastewater treatmet unit operations are used for the removal of organic compounds from hazardous waste and other industrial wastewater streams. Some operations use aeration to supply oxygen for aerobic decomposition of organics; in other operations, incidental air/water contact occurs to varying degrees. Methods for estimating emissions resulting from air stripping of volatile organic compounds that may accompany aerated treatment are applied to full scale and pilot plant wastewater treatment plants.

Treatment plant examples are investigated for aerated industrial waste treatment systems employing trickling filters, activated sludge and aerated lagoons. The size and configuration of full size treatment plants are highly variable, corresponding to the highly variable volume and strength of industrial wastewater. Typical size and residence time specifications for unit operations within these plants are discussed.

The recommended mathematical models are used to generate predictions of the fate of volatile organic compounds in wastewater treatment systems. Where full scale plant data are available, predictions generally agree with measurements (within the limits of accuracy which result from variations in sampling and chemical analysis). For this reason, the mathematical models can be used to estimate emissions for those systems where no field data are available.

This Project Summary was developed for the EPA's Hazardous Waste Engineering 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

The EPA Office of Air Quality Planning and Standards (OAQPS) is developing regulations under the 1976 Resource Conservation and Recovery Act (RCRA) to control air emissions from hazardous treatment, storage, and disposal facilities (TSDFs). The purpose of the air emissions regulations is to protect human health and the environment from emissions of volatile organic compounds (VOCs), particulates, and aerosols.

The sources of TSDF emissions include storage tanks, treatment processes, surface impoundments, lagoons, landfills, land treatment, and drum storage and handling facilities. Those processes involving the use of air (biological treatment and cooling) or subject to the introduction of air (stirred equalization and neutralization) may emit VOCs as a consequence of air stripping.

To further understand and better estimate the sources and extent of VOC emissions from TSDFs, typical aerated treatment facilities are investigated. Various mathematical models are presented to predict the mechanism and extent of VOC emissions during the

different process conditions encountered. The models include a methodology for estimating the relative importance of competing removal pathways (i.e., adsorption and biological oxidation). The study is limited to those biological processes or physical chemical processes with potential to vent VOC to the air.

The basic problem in evaluating air emissions from aerated waste treatment processes is determining the importance of competing mechanisms. In an activated sludge biological treatment process, for example, the major mechanisms for removal of dissolved contaminants from the aqueous waste are biological oxidation, adsorption on biomass, and mass transfer into the air. In a rough analysis of "removal efficiency" concentrations of the contaminants in the aqueous influent and effluent are measured and the fraction of the contaminant which disappears in the process is reported as an efficiency. This procedure gives no information about the relative importance of competing removal mechanisms.

Where one or more of the removal mechanisms is destructive of the contaminants (chemical or biological oxidation) and others non-destructive (air stripping or aerosol dispersal), measuring the relative importance of the competing mechanisms becomes complicated. In such a case, the contaminant removed by the non-destructive mechanism must be recovered and the balance assumed to have been destroyed. Errors in chemical analyses, and particularly sampling errors, have a great impact on calculations of the fraction of the destroyed contaminant.

Alternatively, data may be obtained under controlled laboratory conditions and adapted to provide reasonable estimates of emissions expected under field conditions. One approach is to conduct experiments in covered vessels to permit accurate sampling of vent gases and accurate metering of vent gas flow rates. Another approach involves inhibiting the destructive removal mechanisms by taking steps to chemically sterilize the system or to substitute an inert gas such as nitrogen for air. In this latter case, the mass transfer to the gas phase continues to occur and all of the destructive mechanisms are eliminated. Influent and effluent aqueous phase sampling are used to determine the extent of removal resulting from stripping. Vapor phase sampling of such a laboratory system should close the mass balance for the system. The extent to which under-recovery or over-recovery of contaminants is found can be used to evaluate the adequacy of laboratory vapor phase sampling techniques.

One approach to the air stripping problem is to measure the total disappearance in the field and then apply mathematical models obtained from laboratory data to simultaneously estimate the rate of stripping and biological oxidation. When these models account for significantly more or significantly less contaminant removal than the observed total removal, several steps may be taken. The simplest approach is to assume that the mass transfer model is more accurate than the biological oxidation model and account for biological oxidation (and other destructive removal mechanisms) by difference. Because they are less affected by changes in operating conditions and influent wastewater composition, the mass transfer models are in fact more accurate predictors than are the biological oxidation models. In some cases, however, air sampling must be conducted to verify the prediction of stripping models. The interpretation of such data obtained under field conditions is, however, subject to considerable error.

The objectives of this study are to present and evaluate the various kinetic and predictive fate models that are applicable to aerated wastewater treatment systems. Four different waste treatment systems will be considered: (1) trickling filters, (2) activated sludge, (3) aerated lagoons, and (4) spray ponds. When possible, model predictions will be compared with experimental data.

This study investigated mathematical models and correlations available in the literature for mass transfer in systems similar to wastewater treatment units. Classical engineering approaches to strippers and absorbers, packed bed design, and stream and lake reaeration were considered and adapted as necessary to wastewater treatment systems.

Procedure

Pretreatment was modeled as a plug flow system with the gas phase mass transfer coefficient calculated from a "wind speed" correlation and the liquid phase mass transfer coefficient calculated using a stream reaeration correlation. Primary and secondary clarifiers were modeled as plug flow systems using the same methods as described above to calculate mass transfer coeffi-

cients. Surface aeration systems (e.g. some activated sludge units) were modeled using a correlation with applied aerator horsepower. Biological oxidation was incorporated using a pseudo-first order rate constant to be calculated from the best available zero-order data and an assumption as to steady state composition.

Diffused aeration systems (e.g. some activated sludge systems with submerged aerators) were modeled with stripping based on the attainment of equilibrium during the time of bubble rise, which is combined with surface diffusion calculated as for clarifiers. Biological decay is treated in the same manner regardless of the means of aeration. Suggested procedures for calculating mass transfer coefficients appropriate for equalization ponds, dissolved air flotation units, spray ponds and cooling towers are also given.

As a step in verifying the accuracy of the suggested mathematical models, data from an extensive sampling program at a well characterized (with respect to residence time, dimensions and influent and effluent concentrations) wastewater treatment system were used to test the models. In addition, pilot scale data from well controlled experiments and some less extensive industrial wastewater treatment system data from EPA plant surveys were also used.

A list of input specifications which describe the system to be modeled is given in Table 1; values given are from a wastewater treatment system at a Union Carbide chemical manufacturing plant. For cases where units of a particular type are not used in a particular system (e.g. dissolved air flotation in the example given), a specification of zero for area, number, or air flow eliminate the inappropriate part of the model.

Results and Discussion

The results of the calculations on the sample plant specification are given in Table 2. The rate of loss of volatiles from the plant as predicted by the mathematical models agreed well with measured results, with the exception of the UNOX biological treatment unit. The rate of removal in the UNOX system was overpredicted by the model particularly in the case of tetralin. Although the loss in the aeration basin was overpredicted by the model for tetralin and naphthalene (89% was the observed loss in both cases), the absolute errors were still only 5-10%.

Table 1. Model Input Data for Union Carbide Plant (Alsop, et al., 1984)*

Water Temperature (Deg C)	25
Wind Velocity (cm/S)	200
Concentration of Benzene (Mole Fract)	.001
Concentration of Naphthalene (Mole Fract)	.005
Concentration of Ethylbenzene (Mole Fract)	.001
Concentration of Methylcellosolve (Mole Fract)	.001
Concentration of Tetralin (Mole Fract)	.0002
Biorate of Benzene (Hours)	400
Biorate of Naphthalene (Hours)	400
Biorate of Ethylbenzene (Hours)	400
Biorate of Methylcellosolve (Hours)	800
Biorate of Tetralin (Hours)	200
Waste Flow Rate (M³/Sec)	.07
Area of Pretreatment Basin (M²)	50
Depth of Pretreatment Basin (M)	3
Diameter of Clarifier (M)	19.4
Depth of Clarifier (M)	2.4
Number of Clarifiers	1
Length of Aeration Basin (M)	170
Width of Aeration Basin (M)	170
Depth of Aeration Basin (M)	3.6
Area of Agitators (Each) (M²)	96
Number of Agitators	30
Power of Agitation (Each) (HP)	75
Impeller Diameter (cm)	30
Impeller Rotation (rpm)	2000
Number of Secondary Clarifiers	1
Diameter of Secondary Clarifiers (M)	37
Depth of Secondary Clarifiers (M)	3
Area of Equalization Basin (M²)	5185
Depth of Equalization Basin (M²)	3
Air Flow in DAF (Pretreat) (SM³/S)	0
Flow of Submerged Air (M³/Sec)	.4
Power of Sub-Agitation, Each (HP)	50
Length of Sub. Aeration Basin (M)	33.5
Width of Sub. Aeration Basin (M)	8.4
Depth of Sub. Aeration Basin (M)	8.5
Area of Sub. Agitators (Each) (M²)	70.1
Number of Sub. Units in Series	3
Impeller Rotation (rpm)	70
Impeller Diameter (cm)	243
Weir Height (cm)	30
Thickness of Weir Flow (cm)	1
Enter {1} for Covered Subm. Agit.	1

*Fate of Specific Organics in an Industrial Biological Wastewater Treatment Plant, EPA Draft Report (June 29, 1984).

In an EPA pilot investigation, a number of VOCs were processed in a clarifier before entering an aerated biological oxidation unit. Enough data were provided to specify the input parameters of the model. Although the treatment plant was not directly exposed to the atmosphere, air was circulated and the mass transfer is considered to be liquid phase controlled. For both the clarifier and the aerator, the model predicted VOC losses in close agreement with the pilot data. The model predicted that most of the VOCs were lost to the circulating air.

The fractional loss of VOCs to the air was estimated for the du Pont Belle, WV plant. The model predictions for methanol, acetone, and chloroform were within a factor of 5 for the primary process, but did not agree with the estimated losses of butanol. The secondary treatment estimations did not agree with model predictions. Not enough information was provided to determine the source of the difference. At the Union Carbide Sisterville plant, the predicted fractional loss was within a factor of 5 of the estimated values. Only primary treatment was assumed; except for the flow rate, no information was provided about the source characteristics.

Conclusions and Recommendations

The available theoretical and semi-empirical methods for predicting the rates of mass transfer of volatile organic compounds from dilute solution into air can be used to accurately predict emissions from aerated wastewater treatment processes in the absence of competing removal mechanisms. Where liquid phase concentration data and system operating conditions are well-characterized, VOC emissions from aerated lagoons, activated sludge processes, trikckling filters, and clarifiers associated with wastewater treatment systems may be estimated within the accuracy of sampling and chemical analysis results.

The presence of competing removal mechanisms, of which biooxidation is the most important, reduces the accuracy of emissions predictions based on plant influent concentration data. If bulk wastewater concentrations are known for individual treatment units, then reasonably accurate predictions may be made. However, when only the concentration of the influent to the entire plant is known, accurate rate data for biooxidation become more important, and their absence has a greater influence on the accuracy of emissions estimation.

Biooxidation rate data is available in the literature for various organic compounds which may be present in industrial wastewater. The data are highly dependent on the conditions under which they were obtained and are not easily adapted to real systems which may have different initial concentrations, biomass loadings, nutrient and inhibitor concentrations, etc. A table of bioxidation rate data obtained from the literature is included in the final report to provide a starting point for calculations.

Industrial waste treatment systems vary widely in design reflecting the wide variation in the waste streams to be treated. The recommended predictive mathematical models are adapatable to widely varying volumetric flow rates. Residence time, which in actual system designs accounts for the concentration and increases with the difficulty of removal of organic compounds and suspended solids, must be specified from actual system designs or estimated (less accurately) from removal rate data. Model plant designs are given in the report which fit within the wide range of suitable designs. The best mathematical models, as determined

Table 2. *A Comparison of the Experimental Loss of Volatiles from the Union Carbide Plant Field Test to the Predicted Loss from Mathematical Models*

Unit/Volatile	Fractional Loss (experimental)	Fractional Loss to Air (predicted)
Clarifier Surface		
Benzene		.16
Ethyl Benzene		.15
Toluene		.15
Dichloroethane		.13
Naphthalene		.12
Tetralin		.15
Clarifier Overflow		
Benzene		.01
Ethyl Benzene		.01
Toluene		.01
Dichloroethane		.01
Naphthalene		.006
Tetralin		.01
Total Clarifier		
Benzene	.058	.17
Ethyl Benzene	.103	.16
Toluene	.13	.16
Dichloroethane	.143	.14
Naphthalene	.045	.116
Tetralin	.225	.16
Equalization Basin		
Benzene	.391	.31
Ethyl Benzene	.35	.29
Toluene	.281	.29
Dichloroethane	.389	.31
Naphthalene	.269	.27
Tetralin	.115	.29
Aeration Basin		
Benzene	.9984	.998*
Ethyl Benzene	.993	.997*
Toluene	.993	.998*
Dichloroethane	.987	.994*
Naphthalene	.892	.994*
Tetralin	.905	.998*
UNOX		
Benzene	.26	.58*
Ethyl Benzene	.44	.55*
Toluene	.19	.62*
Dichloroethane	−.08	.23*
Naphthalene	.31	.26*
Tetralin	.05	.73*

Includes biological loss (approximately 0.01)

by this study, were compared with experimental measurements of full-scale and pilot-scale wastewater treatment systems. Sample calculations are included in an Appendix to the final report.

The authors conclude that reliable emissions estimates (i.e., estimates within the accuracy which is expected to result from variations in sampling and chemical analysis) can be made using selected mathematical models and correlations. Where plant operating conditions including residence times, aeration rates, dimensions, etc., are available, limitations in applying the mathematical models result from lack of accurate biooxidation and partition coefficient data. When descriptions of specific plant operating parameters are not available, rough estimates can be made based on model plant designs, adjusting for wastewater flow rates.

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***Ronald J. Turner** is the EPA Project Officer, see below.*

The complete report, entitled "Preliminary Assessment of Air Emissions from Aerated Waste Treatment Systems at Hazardous Waste Treatment Storage and Disposal Facilities," (Order No. PB 87-113 783/AS; Cost: $18.95, subject to change) will be available only from:

> *National Technical Information Service*
> *5285 Port Royal Road*
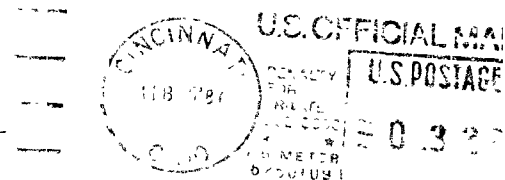> *Springfield, VA 22161*
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