Use of Open-Path FTIR Spectroscopy to Support Development of Refined Estimates of H_2S Emissions from a New York City Municipal Wastewater Treatment Plant

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ABSTRACT

A comprehensive hydrogen sulfide (H_2S) emissions inventory was developed in the summer of 2001 to support a major upgrade of the City of New York's 26th Ward Wastewater Treatment Plant in the Borough of Brooklyn. The goal was to identify emission controls necessary to ensure that strict compliance with hourly, off-site, nuisance-based standards is achieved.

The Area-Source Technique was used to obtain H_2S emission rates from each uncovered process source. A downwind, path-averaged H_2S concentration was derived for each 15-minute "monitoring event." Each event consisted of 34 near-ground (1m height) point measurements using two comparably performing Jerome meters. Emission rates were back-calculated from these concentrations using a Gaussian dispersion model and requisite on-site measurements of wind speed, wind direction, and atmospheric stability. Higher-emitting areas (such as weirs and other turbulent areas) were accounted for in the back-calculations by periodically measuring H_2S at up to 30 representative locations, directly above each source surface, from which relative "hot-spot" source strengths were derived and assigned.

Because the cost of controlling H_2S emissions is likely to be significant for the preliminary settling tanks, several means of reducing the conservatism in the emissions estimation for this source were investigated. Open-path FTIR spectroscopy was utilized along the H_2S measurement path to monitor two tracer gases released in a controlled manner from different upwind locations, thereby facilitating the direct estimation of vertical dispersion coefficients (sigma-z values) across the downwind source dimension. This, in turn, eliminated the need to rely on somewhat crude relationships between atmospheric stability class and sigma-z values. Unique sigma-z curves were developed for each of 77 separate monitoring events and substituted directly into the dispersion model for H_2S emissions back-calculation.

Results are presented, together with a discussion of cost-benefit implications associated with the sigma-z refinement.

INTRODUCTION

The New York City Department of Environmental Protection (DEP), Bureau of Environmental Engineering (BEE), through its engineering consultant, Hazen and Sawyer, P.C., is currently upgrading the 26th Ward Wastewater Treatment Plant (WTP) in the Borough of Brooklyn, New York. The primary goal of this upgrade is to correct a variety of plant deficiencies concerning wastewater and sludge treatment, as well as to improve plant instrumentation and process control capabilities. Included in this upgrade is the continued compliance with State Pollutant Discharge Elimination System (SPDES) permit requirements through the design and construction of these facility-wide improvements which, either indirectly or directly, will also result in a reduction in emissions of air pollutants and other malodorous compounds to the community.

Existing City and State law requires that the upgrade be performed in such a manner as to ensure that applicable environmental standards are met at all times during facility operations. Among the more problematic of these is the ambient air quality standard for hydrogen sulfide (H_2S). The hourly, off-site, nuisance-based H_2S standard is 10 parts per billion (ppb) in general, and 1 ppb for "sensitive" receptors such as residences and schools. These standards are very strict, and the cost of controlling emissions can easily run into tens of millions of dollars. Therefore, it is in the DEP's best interest to ensure that the emissions inventory upon which the compliance assessment is based is as accurate as possible. It is also important to generate emissions data over a range of facility operating conditions in order to quantify the reduction resulting from the upgrade itself and, correspondingly, to avoid costly over-engineering of controls.

The Area-Source Technique[1] was employed for all uncovered area-type sources (preliminary settling tanks, aeration tanks, and final settling tanks). This technique involves identification of source attribution based on a series of upwind and downwind point measurements averaged along pre-specified measurement paths, and the subsequent back-calculation of emission rates based on careful consideration of established Gaussian dispersion relationships together with use of requisite on-site meteorological data.

Hand-held instruments (Jerome meters) were used for all H_2S measurements. Two instruments were employed simultaneously to generate each crosswind, path-averaged concentration. Beginning at opposite ends of the measurement path, individual readings were taken at 17 equispaced points from which a single path-averaged concentration was calculated. Use of two instruments in this manner reduced the chance of a bias being introduced into the calculated path-averaged concentration owing to lateral meander of the plume centerline over the measurement period. Timing of the measurements was carefully controlled to ensure that each path-averaged concentration was collected over a span of precisely 15 minutes. Each 15-minute period of 34 H_2S measurements is referred to as a "monitoring event" and is identified as a numbered pair to reflect the contribution from each Jerome meter.

One of the limitations of the Area-Source Technique involves the need to consider atmospheric stability class for assignment of vertical dispersion coefficients (sigma-z values) in the model employed for emissions back-calculation. Each atmospheric stability class is associated with a discrete curve which presents sigma-z as a function of downwind distance. This quantum (or step-type) treatment of vertical dispersion is necessarily reflected in the emissions back-calculation. Implications of this limitation are most significant for the preliminary settling tanks, as H_2S emissions are greatest from this source. Accordingly, special attention was focused upon this source and the data-collection program was enhanced.

The accuracy of the emissions back-calculations for the preliminary settling tanks was improved significantly by collecting data to allow for the direct calculation of sigma-z. Open-path FTIR spectroscopy was utilized along the H_2S measurement path to monitor two tracer gases -- carbon tetrafluoride (CF_4) and sulfur hexafluoride (SF_6) -- released in a controlled manner from different upwind locations, thereby facilitating the direct calculation of sigma-z across the downwind source dimension. Unique sigma-z curves were developed for each monitoring event for this source and substituted directly into the dispersion model for H_2S emissions back-calculation. This precluded the need to explicitly consider atmospheric stability and, in turn, eliminated the error caused by the inability to parameterize vertical dispersion as a continuous function.

All monitoring events for the preliminary settling tanks took place during 9 days between July 9 and August 9, 2001. Data from 84 monitoring events were collected, but 7 were eliminated due to tracer-gas flow problems or unacceptable plume capture arising from oblique wind directions.

Meteorological forecasting was employed to predict those days when the direction of the wind was most likely to be within acceptable "windows," identified in advance based on logistical considerations.

Emphasis was placed on collecting emissions data during times of dry-weather flow, i.e., during those conditions, within the normal range of plant operating limits, likely to enhance anaerobic (septic) conditions necessary for H_2S generation. Data was collected during the summer when influent temperatures were at their annual peak, as anaerobic activity is directly proportional to influent temperature.

METHODOLOGY

Methodologies relating to the instrumentation employed, the Area-Source Technique, and the treatment of vertical dispersion are discussed below.

Instrumentation

Jerome H$_2$S Analyzer

The Jerome Model 631-X Analyzer (Jerome meter) employs a gold film sensor which, in the presence of varying H$_2$S concentrations, undergoes changes in electrical resistivity. This model also employs a dilution system which permits operation over four concentration ranges, the lowest of which allows a sensitivity to 3 ppb. H$_2$S measurements are reported based on "total" reduced sulfur representing the actual H$_2$S present, plus low-molecular-weight mercaptans, thereby providing concentrations which may be somewhat conservative.

The Jerome meter can measure H$_2$S in real time (a response time on the order of about 20 or 30 seconds) to levels as low as 1 ppb. When the sample button on the unit is pressed, an internal pump draws air into the instrument where it is analyzed. The electrical potential across the gold film is continually monitored, and the concentration is shown by means of a digital display where it remains until the next sample is taken.

FTIR Spectrometer

The open-path FTIR spectrometer employed was an AIL Systems RAM2000 Remote Air Monitor. Open-path FTIR spectroscopy is able to provide real-time, simultaneous analysis of up to several dozen gaseous contaminants. The technology is identical in principle to classical laboratory FTIR spectroscopy, except the cell from which a sample is measured is essentially extended to the open atmosphere. A beam of light spanning a range of wavelengths in the near-IR portion of the electromagnetic spectrum (approximately 2 to 14 microns) is propagated from the transmitter portion of the instrument. In the most common configuration, a "retroreflector," comprised of an array of corner-cubed mirrors, is positioned to intercept this radiation and redirect it back upon itself to the receiver portion of the instrument.

An interferometer splits the returning beam of radiation into two paths and then recombines them in a way to generate an interference from the phase differences. The phase difference, and thus the interference, is dependent on the wavelengths present in the beam. In one of the paths, the radiation is reflected off a moving mirror, resulting in an intensity variation which is measured as a function of the path difference between the two mirrors. The result is an interferogram.

The interferogram obtained from a monochromatic beam is simply a cosine wave. The broadband interferogram is a sum of cosine waves (the Fourier series) for each spectral component as a function of mirror pathlength separation. A spectrum in the optical frequency units, cm^{-1}, is obtained by performing a Fourier transform upon the interferogram.

Contaminants of concern are identified and quantified via a computer-based spectral search involving sequential, compound-specific analysis and comparison to the system's internal

reference spectra library. The most widely employed technique for analyzing FTIR spectral data is the multicomponent classical least squares (CLS) technique. Any gaseous compound which absorbs in the IR region is a potential candidate for monitoring using this technology.

Resultant path-integrated concentrations are typically reported in units of parts-per-million-meters (ppm-m). It is often necessary to convert path-integrated concentrations (ppm-m) to units of milligrams per cubic meter times meter (mg/m^3 x m) or mg/m^2. Generation of a path-integrated concentration yields contaminant information along the entire pathlength and not just at a single point (or collection of points) in space as with traditional point-monitoring methods.

Tracer-Gas Release System
Separate tracer-gas release systems were employed to release CF_4 and SF_6 at controlled, uniform rates, coincident with each 15-minute monitoring event for the preliminary settling tanks.

Each tracer-gas release system included a cylinder of 99% pure compound which was delivered through a multistage regulator to a calibrated rotameter. Each rotameter was compound-specific with multipoint CF_4 and SF_6 calibration curves. In each system, the gas exited the multistage regulator and traveled through 10 or 20 feet of Teflon tubing to a delivery system consisting of the rotameter, a funnel, and a ring stand.

Meteorological Systems
Two meteorological systems were employed for this investigation. The first system was a portable tower equipped to monitor wind speed at a height of 1 meter above the ground. The second system was a 10-meter tower (temporary installation) equipped to monitor wind speed, wind direction, sigma-theta (standard deviation of the horizontal wind direction), and solar radiation at a height of 10 meters, and delta temperature between 2 and 10 meters.

The portable 1-meter system was set up and operated at an on-site location judged representative of the microscale meteorology in the region between the source and the respective measurements. The 10-meter system was installed at an on-site location representative of the local meteorology as influenced by the facility and its immediate environs.

Each system was calibrated and maintained in conformance with requirements set forth in the USEPA document, Meteorological Monitoring Guidance for Regulatory Modeling Applications.[2] All meteorological data was collected in user-defined, 15-minute blocks with capabilities for real-time, in-field display (both instantaneous and 15-minute-averaged). Additionally, for any given 15-minute period, capabilities existed for the display of 5-minute-averaged data.

All meteorological equipment was manufactured by Climatronics Corporation. Model F-460 wind speed and wind direction sensors were used on each system. These consist of three-cup anemometers with variable frequency output and variable-voltage wind direction sensors with balanced magnesium vanes. Delta temperature was measured using variable-resistance dual thermistors in stainless steel sheaths and housed in motor-aspirated shields.

Area-Source Technique

The Area-Source Technique is applicable to all area-type sources, i.e., homogeneous sources (uniformly emitting) and non-homogeneous sources (having "hot spots"). It involves identification of a source "attribution" based on a series of near-ground (1m height) upwind and downwind measurements and the subsequent back-calculation of emission rates based on Gaussian dispersion relationships inherent in most USEPA Guideline models (e.g., ISCST). In addition to the source-attribution information, coincident on-site measurements of wind speed, wind direction, and parameters relating to atmospheric dispersion are required.

Source-attribution is represented as a path-integrated concentration and is obtained by subtracting the upwind path-integrated concentration from the downwind path-integrated concentration. Mathematically, a path-integrated concentration (units of mg/m^2) can be derived by integrating a concentration at a point (mg/m^3) across the width (crosswind direction) of the plume (m). The benefit of working with path-integrated (or cross-plume) concentrations lies in the inherent spatial representativeness of the data.

Ideally, path-integrated measurements are generated via some type of optical remote sensing technique -- such as open-path infrared (IR) or ultraviolet (UV) spectroscopy -- which yields such data directly. However, H_2S is a notoriously poor absorber of IR and UV radiation and, as a result, associated minimum detection levels were not sufficient to meet the measurement quality objectives required for the program. Therefore, a source-attribution approach based on use of rapid-response point monitors (Jerome meters) was employed in which multiple measurements were taken along the downwind (cross-plume) path.

The Area-Source Technique has been accepted in regulatory applications by USEPA and is consistent with applicable USEPA guidance.[3] The technique, as modified for use with point monitors, is as follows:

1.   Identify Source Attribution

This step consists of a series of 15-minute-averaged monitoring events in which concurrent (or sequential), near-ground-level H_2S measurements are made upwind and immediately downwind of the source to identify source attribution. Downwind measurements are made at pre-designated locations equispaced along the downwind source perimeters. Wind speed, wind direction, and atmospheric stability class are averaged over each monitoring event.

2.   Predict Relative Path-Integrated Concentration Along Measurement Path

This step consists of using an appropriate dispersion model to predict the relative path-integrated concentration along the downwind measurement path defined in Step 1. This is accomplished by: (a) predicting the point concentration (mg/m^3) at every meter along the measurement path based on a unity emission rate (e.g., 1 mg/m^3) and actual meteorology and source configuration; (b) determining the arithmetic average of the point concentrations (mg/m^3); and (c) multiplying the average point concentration by the downwind pathlength (m).

For this work, the USEPA Industrial Source Complex Short-Term Dispersion Model, Version 3 (00101, LF90 Version 4.52, 4/27/00), hereafter referred to as the ISCST3 Model, was utilized, in urban mode, using regulatory default options with a flat-terrain approach.

Process-tank "hot spots" were represented in the unity modeling by assigning a scalar multiplier to the appropriate subarea of the source. This scalar multiplier was based on results of hot-spot monitoring (also using the Jerome meter) during the source-attribution monitoring program.

3.   Scale Unity Modeling Results to Estimate Emission Rate

This step involves estimating the actual emission rate, Q_A, in accordance with the following ratio (Equation 1):

$$\frac{C_M}{Q_A} = \frac{C_P}{Q_U}$$

where:

C_M = measured path-integrated H$_2$S concentration (attribution) (mg/m^2)
Q_A = actual H$_2$S emission rate (mg/m^2-s)
C_P = predicted relative path-integrated concentration (mg/m^2)
Q_U = unity-based emission rate (mg/m^2-s)

Treatment of Vertical Dispersion

Discussed below are both the initial and refined treatments of vertical dispersion.

Initial Treatment

The initial treatment of vertical dispersion required assignment of an atmospheric stability class for each 15-minute event to support the H$_2$S emissions back-calculation process. For a given downwind, path-averaged concentration, the associated emission rate is dependent upon how much H$_2$S has dispersed in the vertical, above the source, prior to reaching the instrument.

In Gaussian theory, the amount of H$_2$S lost in the vertical can be estimated through knowledge of the vertical dispersion coefficient, which may be thought of as the height one would have to go above a plume centerline before the concentration is reduced by a factor of 1/e, or about 36.8%. Sigma-z increases with increasing downwind distance from the source.

Because sigma-z is difficult to measure, it is generally approximated based on consideration of atmospheric stability class. For dispersion modeling purposes, stability classes A through F are typically identified, in which Class A is the least stable (large sigma-z values) and Class F is the most stable (small sigma-z values). For each stability class, a unique formula is used to assign a sigma-z value as a function of downwind distance.

A stability class was assigned to each monitoring event based on employment of the sigma-theta (standard deviation of the horizontal wind direction or σ_θ) method. A detailed description of this method can be found in Section 6 of the earlier-referenced USEPA monitoring guidance document,[2] and is not reproduced herein.

Refined Treatment
As discussed earlier, limiting the vertical dispersion coefficient to one of six discrete values for a given downwind distance represents a simplification in the emissions back-calculation process, as vertical dispersion is actually a continuous function. Further, there are meteorological conditions under which the above methods for stability class assignment may err on the conservative side; i.e., may overestimate sigma-z values, thus overestimating H_2S emissions.

The tracer method was employed to measure vertical dispersion coefficients on an event-specific basis. This method makes use of the crosswind-integrated form of Turner's general Gaussian equation for ground-level concentration downwind of a continuously emitting, ground-level point source:

$$\sigma_z \ = \ (2\pi)^{\frac{1}{2}} \, Q \, (\pi C u)^{-1} \qquad \text{(Equation 2)}$$

where:

σ_z = vertical dispersion coefficient at the particular downwind distance (m)
Q = uniform tracer-gas emission rate (g/s)
C = ground-level crosswind-integrated tracer-gas concentration (g/m^2)
u = mean wind speed (m/s)

The method involved release of small amounts of CF_4 and SF_6 at controlled flow rates, each from an elevation of 1 meter, from locations 22.3 meters and 46.9 meters, respectively, upwind of the FTIR beam path. These tracer gases were monitored as path-integrated concentrations, immediately downwind of the source, using open-path FTIR spectroscopy in accordance with USEPA Toxic Organic Compendium Method 16 (Method TO-16).

In order to accommodate winds from a southerly quadrant, the transmitter and retroreflector were positioned in a plant east-west orientation, about 1 meter north of the source's northern boundary during all measurements (i.e., in close proximity to the downwind Jerome meter measurement path). The beam pathlength (one-way) was 81.5 meters, and the beam was positioned at a height to coincide, as nearly as possible, with the height of the Jerome meter sampling locations (about 1 meter off the ground).

RESULTS AND DISCUSSION

Because of space limitations and the large volume of data collected, results are arbitrarily presented for only 8 of the 77 valid monitoring events performed (the first 8 events of August 6).

Tables 1 and 2 present the sigma-z calculations based on the CF_4 and SF_6 data, respectively, for the preliminary settling tanks.

Table 1. Sigma-z Calculations Based on Carbon Tetrafluoride Data

	Meteorology					Initial σz @ 22.3m (m)	Adjusted Downwind Distance (m)	Plume-Capture Adjustment		
Event	10m WD (º)	10m $\sigma\theta$ (º)	1m WS (m/s)	CF_4 Conc. (g/m²)	Q (g/s)			Plume Capture (%)	Adjusted CF_4 Conc. (g/m²)	Final σz (m)
169, 70	181	13.7	2.9	0.00767	0.0380	1.36	22.3	100.0	0.00767	1.36
171, 72	199	17.3	2.4	0.00748	0.0380	1.68	23.6	100.0	0.00748	1.68
173, 74	210	14.1	2.2	0.00690	0.0380	1.97	25.8	100.0	0.00690	1.97
175, 76	206	17.0	2.2	0.00691	0.0380	2.00	24.8	100.0	0.00691	2.00
177, 78	184	8.0	2.6	0.00667	0.0380	1.75	22.4	100.0	0.00667	1.75
179, 80	187	8.3	2.9	0.00657	0.0380	1.61	22.5	100.0	0.00657	1.61
181, 82	184	9.2	2.5	0.00550	0.0380	2.20	22.4	100.0	0.00550	2.20
183, 84	181	9.8	2.2	0.00485	0.0380	2.85	22.3	100.0	0.00485	2.85

Table 2. Sigma-z Calculations Based on Sulfur Hexafluoride Data

	Meteorology					Initial σz @ 46.9m (m)	Adjusted Downwind Distance (m)	Plume-Capture Adjustment		
Event	10m WD (º)	10m $\sigma\theta$ (º)	1m WS (m/s)	SF_6 Conc. (g/m²)	Q (g/s)			Plume Capture (%)	Adjusted SF_6 Conc. (g/m²)	Final σz (m)
169, 70	181	13.7	2.9	0.01657	0.1087	1.80	46.9	100.0	0.01657	1.80
171, 72	199	17.3	2.4	0.01460	0.1087	2.46	49.6	100.0	0.01460	2.46
173, 74	210	14.1	2.2	0.01497	0.1087	2.59	54.2	97.1	0.01542	2.52
175, 76	206	17.0	2.2	0.01340	0.1087	2.95	52.2	99.5	0.01347	2.94
177, 78	184	8.0	2.6	0.01268	0.1087	2.64	47.0	100.0	0.01268	2.64
179, 80	187	8.3	2.9	0.01416	0.1087	2.14	47.3	100.0	0.01416	2.14
181, 82	184	9.2	2.5	0.01172	0.1087	2.96	47.0	100.0	0.01172	2.96
183, 84	181	9.8	2.2	0.00763	0.1087	5.19	46.9	100.0	0.00763	5.19

Initial sigma-z (σ_z) values in Tables 1 and 2 are presented for each 15-minute monitoring event based on the crosswind-integrated form of Turner's equation (Equation 2) and assuming that the wind is perpendicular to the beam path (i.e., from plant south or 180º).

Based on the departure of mean (actual) 10-meter wind direction from normal, adjustments were made to the distances downwind of the tracers at which each sigma-z value applies. This was accomplished by dividing the normal downwind distances of the tracers (22.3 and 46.9 meters) by the cosine of the absolute value of the difference between the mean wind direction and 180º.

Plume-capture of the tracer gases was assessed by modeling selected events using actual meteorology. Plume-capture adjustments were made, as required, to account for the fact that the FTIR beam was not always long enough to capture the outer edges of the tracer plumes owing to the departure from normal of the mean wind direction and to horizontal dispersion. Incomplete plume capture occurred most often for SF_6, as this was the tracer released furthest upwind.

Plume-capture assessment required appropriate treatment of atmospheric stability (i.e., horizontal and vertical dispersion) in the model. For CF_4, this involved use of the horizontal and vertical dispersion coefficients based on the P-G stability class as determined for each event using the sigma-theta method. For SF_6, this also involved use of the horizontal and vertical dispersion coefficients based on the P-G stability class; however, in this case, the P-G stability class was assigned to each event using the CF_4-based sigma-z data (vs. the sigma-theta method), as it utilized measured vertical dispersion coefficients across the source. The model was then configured to predict concentrations at every meter along the beam path (and along appropriate beam-path extensions), and plume-capture estimates were made for each event by dividing the path-averaged concentration along the beam by the path-averaged concentration along the entire crosswind direction of the plume.

Adjustments were made to the CF_4 and SF_6 concentrations for each event simply by dividing the measured value by the percent plume capture.

Final sigma-z values were calculated for each event by substituting the adjusted concentration (CF_4 or SF_6) into Equation 2.

Table 3 presents the derivation of event-specific sigma-z curves for substitution into the model used for H_2S emission-rate back-calculation. These curves were developed using the CF_4 and SF_6 data, and are specifically limited to the region across the preliminary settling tanks.

Table 3. Derivation of Event-Specific Sigma-z Curves

| | Sigma-Z Data | | | | | |
| Event | CF$_4$-Based (m) | | SF$_6$-Based (m) | | Coefficients (y=ax^2 +bx) | |
	Value	Distance	Value	Distance	a	b
169, 70	1.36	22.3	1.80	46.9	- 0.000919	0.081480
171, 72	1.68	23.6	2.46	49.6	- 0.000830	0.090783
173, 74	1.97	25.8	2.52	54.2	- 0.001051	0.103485
175, 76	2.00	24.8	2.94	52.2	- 0.000888	0.102660
177, 78	1.75	22.4	2.64	47.0	- 0.000892	0.098116
179, 80	1.61	22.5	2.14	47.3	- 0.001061	0.095428
181, 82	2.20	22.4	2.96	47.0	- 0.001432	0.130299
183, 84	2.85	22.3	5.19	46.9	- 0.000697	0.143342

The final CF$_4$- and SF$_6$-based sigma-z values and adjusted downwind distances (from Tables 1 and 2, respectively) are presented in Table 3 for each event. Also presented are the coefficients ("a" and "b") from the second-degree polynomial ($y = ax^2 + bx + c$) used to represent each curve, where "y" equals the sigma-z value at some downwind distance "x," and "c" is set equal to zero.

A second-degree polynomial was identified as the equation of choice, as it represents the simplest function which can be constructed to pass through the three known points on the curve (the origin and the two sigma-z measurement points). Because this function is used only to support the emissions back-calculation, we chose this strictly empirical approach to represent vertical dispersion within the very limited region between the upwind edge of the source and the downwind emissions-assessment measurement path. This avoids the need to address complex dispersion modeling issues and associated theoretical assumptions about the shape of the curve within this region.

Parameterization of sigma-z for modeling purposes is generally accomplished using an approach which applies some type of power law equation to an array of observed measurements at distances between several hundred meters and a few kilometers downwind of a source. Such representations yield sigma-z curves which are concave in form in order to take into account the fact that sigma-z must always increase with downwind distance.

In contrast, for all monitoring events shown in Table 3 (and for all but 2 of the 77 for the entire program), the curve is convex as evidenced by the sign of the "a" coefficient in the equation. Second-order polynomials having a negative "a" coefficient must, at some downwind distance, have a maximum beyond which the sigma-z value actually decreases with downwind distance.

Nearly all of the 77 valid events occurred during a sea breeze situation, including the 8 events presented in these tables. The observed sigma-z data provides overwhelming evidence of the role of mechanically induced turbulence over the preliminary settling tanks in this very stable sea breeze regime. This phenomenon, not accounted for in the model's extrapolation of sigma-z curves to downwind distances less than 100 meters, is clearly evidenced by CF_4-based sigma-z values which are large compared to the SF_6-based sigma-z values (and by the corresponding form of the resultant second-order polynomial).

Table 4 presents the emission-rate determinations for the preliminary settling tanks based on use of the measured vertical dispersion coefficients.

Table 4. Emission-Rate Determinations Using Measured Vertical Dispersion Coefficients

| Event | Unity ISCST3 Analysis | | Meteorology | | | | Measured Source Attrib. (g/m^2) | Actual Emission Rate (g/s) | | |
	Emission Rate (g/s)	Predicted Source Attrib. (g/m^2)	10m WD (º)	1m WS (m/s)	P-G Stab. Class	Temp. (ºK)		Quiescent Areas	Turbulent Areas	Total
169, 70	2.020521	0.250658	181	2.9	E-F	302.9	0.0135936	0.0182	0.0913	0.1096
171, 72	2.020521	0.236499	199	2.4	E-F	303.0	0.0132030	0.0188	0.0940	0.1128
173, 74	2.020521	0.234533	210	2.2	E-F	303.0	0.0128387	0.0184	0.0922	0.1106
175, 76	2.020521	0.220854	206	2.2	E-F	303.2	0.0075912	0.0116	0.0579	0.0694
177, 78	2.020521	0.222234	184	2.6	E-F	303.2	0.0142833	0.0216	0.1083	0.1299
179, 80	2.020521	0.221378	187	2.9	E-F	302.8	0.0113557	0.0172	0.0864	0.1036
181, 82	2.020521	0.204321	184	2.5	E-F	303.0	0.0109493	0.0180	0.0903	0.1083
183, 84	2.020521	0.160049	181	2.2	D	303.2	0.0066867	0.0140	0.0704	0.0844

In Table 4, the emission rate used in the unity ISCST3 analysis was derived by considering a unity emission rate of 0.0001 $g/s\text{-}m^2$ over the quiescent areas (carefully calculated to be 3,362.38 m^2) together with a "hot-spot-adjusted" unity emission rate of 0.00976 $g/s\text{-}m^2$ over the turbulent areas (carefully calculated to be 172.57 m^2), which yielded a total unity-based emission rate of 2.020521 g/s (0.336238 g/s + 1.684283 g/s). The "hot-spot-adjusted" unity emission rate of 0.00976 $g/s\text{-}m^2$ was derived based on results of a comprehensive hot-spot measurement program, in which the average H_2S concentration immediately above the weir (turbulent) areas (17 locations) was 97.6 times greater than the average concentration over the remaining (quiescent) areas (10 locations).

The predicted unity-based source attribution was obtained by running the ISCST3 Model with the above source strengths and configurations for the actual meteorology presented. This included incorporation of a new subroutine into the ISCST3 Model to allow for emissions back-

calculation based on the event-specific sigma-z curves. As discussed earlier, the P-G stability class (assigned using the CF_4-based sigma-z data) was required for treating horizontal dispersion in the model.

The predicted unity-based source attribution may be thought of as the path-integrated concentration which would result based on a source emission of unity for the quiescent areas and 97.6 times unity for the turbulent (weir) areas.

Each measured source attribution was derived by subtracting the upwind from the corresponding downwind path-averaged H_2S concentration (Jerome meter measurements).

The total actual emission rate was obtained by arranging Equation 1 to solve for the actual emission rate (Q_A).

Finally, the apportionment of the quiescent areas and the turbulent areas to the total emissions was derived by adjusting the total emissions in proportion to the unity-based emission rates for these areas. For example, for Event 169-170, the actual emission rate for the quiescent areas is (0.336238 g/s ÷ 2.020521 g/s) x 0.1096 g/s = 0.0182 g/s. Similarly, the actual emission rate for the turbulent areas is (1.684283 g/s ÷ 2.020521 g/s) x 0.1096 g/s = 0.0913 g/s. This source-strength apportionment was necessary to support subsequent dispersion modeling efforts for assessment of off-site H_2S impact.

Table 5 presents the emission-rate reduction based on employment of site-specific sigma-z curves for the preliminary settling tanks.

Table 5. Emission-Rate Reduction Based on Employment of Site-Specific Sigma-z Curves

| Event | Emission Rate (g/s) | | Emission-Rate Reduction (%) |
	Traditional σ_z Treatment	Site-Specific σ_z Curves	
169, 70	0.2619	0.1096	58.2
171, 72	0.3146	0.1128	64.1
173, 74	0.2273	0.1106	51.3
175, 76	0.1758	0.0694	60.5
177, 78	0.2477	0.1299	47.6
179, 80	0.2218	0.1036	53.3
181, 82	0.1826	0.1083	40.7
183, 84	0.0977	0.0844	13.6
Average	**0.2162**	**0.1036**	**52.1**

For the events shown in Table 5, the reduction in emissions realized by the employment of site-specific sigma-z curves averaged 52.1%, and ranged from 13.6 to 64.1%. Although not depicted here, the average reduction over all 77 events was 52.5%, and the range was 13.6 to 69.7%.

CONCLUSIONS

Two main conclusions may be drawn from the preceding results:

- Huge cost savings associated with the wastewater treatment plant upgrade will be realized with respect to the need for emission controls

- In general, traditional methods for assessing atmospheric stability in the presence of a sea breeze environment are likely to result in a gross over-estimation of vertical dispersion

Each of these conclusions is discussed below.

Cost Savings

The value of the open-path FTIR spectroscopy component of the program was clearly evidenced, as the need for emission controls for the preliminary settling tanks will be greatly reduced based on employment of site-specific sigma-z curves in the emissions estimation. Although the dispersion modeling for off-site compliance determination has not yet been completed for this source, it is likely that H_2S emissions from only the weir areas will need to be controlled.

At this time, based on the emissions-refinement work, the savings in capital costs alone associated with H_2S emission controls for this source is conservatively estimated to be between $5 million and $15 million.

There is every reason to believe that this technology can be applied, in a similar manner, to other wastewater treatment plants which have problems in achieving compliance with strict off-site H_2S standards.

Over-Estimation of Vertical Dispersion

Table 6 presents the assignment of P-G stability class based on the SRDT (solar radiation / delta temperature) method and the sigma-theta method for the above eight events.

Table 7 presents the assignment of P-G stability class using the SF_6-based sigma-z data.

Table 6. Assignment of P-G Stability Class Based on the SRDT and Sigma-Theta Methods

| Event | Meteorology | | | | | | |
| | Solar Radiation (W/m^2) | ΔT (ºF) | 10m WD (º) | 10m WS (m/s) | σ_θ @ 10m (º) | P-G Stability Class Assignment | |
						SRDT	Sigma-Theta
169, 70	702	− 2.5	181	3.7	13.7	B	D
171, 72	714	− 2.3	199	3.0	17.3	B	C
173, 74	732	− 2.3	210	3.3	14.1	B	D
175, 76	738	− 2.0	206	3.2	17.0	B	C
177, 78	726	− 2.3	184	4.4	8.0	B	D
179, 80	725	− 2.4	187	4.9	8.3	B	D
181, 82	704	− 2.3	184	4.5	9.2	B	D
183, 84	699	− 2.3	181	4.6	9.8	B	D

Table 7. Assignment of P-G Stability Class Using the SF$_6$-Based Sigma-z Data

| Event | 10m WD (º) | Adjusted Downwind Distance, x (m) | Textbook Sigma-Z Value as a Function of Stability Class | | | | Measured σ_z (m) | Modeled P-G Stability Class |
			A - B	C	D	E - F		
169, 70	181	46.9	11.52	9.38	6.52	3.63	1.80	E - F
171, 72	199	49.6	12.20	9.92	6.89	3.83	2.46	E - F
173, 74	210	54.2	13.34	10.83	7.52	4.17	2.52	E - F
175, 76	206	52.2	12.85	10.44	7.25	4.02	2.94	E - F
177, 78	184	47.0	11.55	9.40	6.54	3.64	2.64	E - F
179, 80	187	47.3	11.61	9.45	6.57	3.65	2.14	E - F
181, 82	184	47.0	11.55	9.40	6.54	3.64	2.96	E - F
183, 84	181	46.9	11.52	9.38	6.52	3.63	5.19	D

In Table 6, the SRDT method of estimating P-G stability class involves consideration of insolation intensity and surface (10-meter) wind speed during the daytime, and vertical temperature gradient and surface wind speed during the nighttime. The sigma-theta method involves consideration of the standard deviation of the wind direction and the surface wind speed (daytime and nighttime). For this investigation, the traditional treatment of sigma-z for emission

calculations used P-G stability classes based on the sigma-theta method.

In Table 7, the measured SF_6-based sigma-z value was considerably smaller than the lowest sigma-z value under the most stable situation allowed by the model (Stability Class E-F based on Briggs vertical dispersion coefficients in the urban mode) for all but one event (183-184). In fact, the measured sigma-z values were smaller than the lowest allowable modeled values in all but 9 of the 77 events for which an SF_6-based sigma-z value was measured.

Tables 6 and 7 illustrate the inappropriateness of using traditional methods (especially the SRDT method during the daytime when all preliminary settling tank measurements were made) for assignment of vertical dispersion coefficients in a sea breeze environment, which was observed during nearly every monitoring event. This can have very significant implications with respect to regulatory-based dispersion modeling, as off-site impacts can be over-estimated for a given emission rate.

ACKNOWLEDGMENTS

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