Wind Transport of Odors and Hazardous Materials

Seminar/Workshop on WIND ENGINEERING
THE PAST TO THE FUTURE

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WIND TRANSPORT OF ODORS AND HAZARDOUS MATERIALS

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Three major hazards to life--fire, explosion and toxic release--usually involve the emission of material from containment followed by vaporization and dispersion. Toxic and flammable materials are characterized by hazards over short time scales as opposed to air pollutants assumed to cause long-term health, corrosion or environmental deterioration. Such materials include noxious or odorous compounds, flammable gases, asphyxiates, and toxic chemicals. Often a hazardous phase is proceeded by odors which are detectable at levels below hazard concentrations. At one time an accepted engineering strategy was to identify hazards by building one chemical facility and waiting to see what happens. This approach was based on the idea "every dog is allowed one bite." But it is no longer seems reasonable to keep dogs as big as Flixborough or Bhopal!

The number and consequence of major chemical spills has increased steadily for the last twenty years. A bypass failure released Cyclohexane at Flixborough, England, in 1974 causing 28 deaths; a Proylene release from a pipeline rupture at a refinery in Beek, Netherlands, in 1975 killed 14; a runaway reaction scattered toxic Dioxin over several square kilometers in Seveso, Italy, in 1976; a tank truck crash in San Carlos, Spain, in 1978 caused a Propylene explosion which killed more than 200; the natural gas explosion in Mexico City left 450 dead; and during the Spring of 1984 in Bhopal, India, toxic fumes killed over 2500.

Buckley and Wiener (1978) examined over 15,000 incidents which occurred in the early 1970's to identify the type, cause, operational area and severity of hazardous releases. They concluded the primary spill causes were tank rupture or puncture; tank overflow; hose or transfer system failure; and non-tank related ruptures (ie. cans, drums, bottles). The most hazardous releases primarily occurred from chemical plant storage or process areas followed by transportation and loading/unloading accidents. But most accidents occurred during transit (57%) and loading/unloading (25%). The most frequently released chemicals were sulfuric acid, ammonium nitrate fertilizer, sodium hydroxide, hydrochloric acid and ethyl parathion. The materials with highest hazard potential reported were anhydrous ammonia, toluene, nitric acid, phenol, methyl alcohol, and xylene. Lees (1980) also summarized the details of an extensive list of hazardous chemical accidents.

Concern over the extent of hazards associated with material spills or process releases has led to a number of field-scale experiments since 1966. Most of these studies involved the release of relatively small quantities of fluid ($\leq 3\ m^3$ of liquid/test); however, since 1980 spills of ammonia, propane, LNG, and Freon-air mixtures have considered liquid quantities from 5 to 40 m^3 (Puttock et al., 1982; McQuaid and Roebuck, 1985) which can generate undiluted gas clouds up to 24,000 m^3 in size! Unfortunately, only a limited subgroup of these tests exhibited the strong negative buoyancy effects which act to accentuate hazards in space and time. These tests have provided some valuable information about the effects of cloud density, release configuration, vapor barrier fences and background atmospheric turbulence on dilution rates. Further information is needed concerning terrain effects, the effectiveness of mitigation devices, chemically reactive clouds, and the initial dilution which occurs during explosive decompression of tank containers and pipelines.

Laboratory scaling of the dispersion of hazardous gas clouds has contributed valuable information about the statistical character of instantaneous releases (Hall et al, 1974, 1979, 1982; Meroney and Lohmeyer, 1983; Davies and Inman, 1986), the interaction of clouds with barriers and fences (Kothari and Meroney, 1981, 1982), and the efficacy of mitigation devices (Meroney, et al., 1984). Meroney (1985) and Davies and Inman (1986) compared data from laboratory simulations of some 60 separate field tests to prototype measurements. They achieved generally "good to excellent" model/full-scale comparisons. They concluded that wind-tunnel simulations of gas cloud dispersion, and simulations of the reduction in concentrations due to vapor fences, sprays and other obstructions provide reliable design and guideline information.

Validation experiments specifically found that:

™ Model and field experiments produced clouds which are very similar in appearance, spread and travel at correct rates, produce comparable concentrations and model peak concentrations are predicted to within a factor of two or better.

™ Field/fluid model comparisons suggest that LFL (lower flammability distances) for cryogenic spills released over land or water are predicted within a standard deviation of 23% with a 90% confidence level.

™ Field/fluid model comparisons suggest that suddenly produced gas clouds which undergo strong initial gravity slumping showed no effective lower threshold of Peclet/Richardson number ratio below which fluid-model concentrations predictions become non-conservative.

™ For trials involving sharp-edged mixing elements there was no evident lower validity threshold of the simulation Reynolds number.

A variety of numerical and analytical models have been proposed to predict the life-history of hazardous gas clouds. Blackmore et al (1982) suggested that these models may be broadly classified into K-theory and slab models. Meroney (1984) suggested five categories of increasing sophistication and plume physics: a) modified Gaussian plume formulae, b) gravitational spread models for pre-entrainment shape, c) volume-integrated box models, d) depth-or cross-section averaged slab models, and e) direct solution of the full three-dimensional conservation equations by finite difference or finite element methods. Wheatley and Webber (1984) considered some 45 numerical models designed to predict dense gas dispersion. They found all-to-often that the models failed to include correct or consistent fluid physics for all physical effects of importance within the range of scales being considered. Recently, Havens and Spicer (1985) proposed a validated cross-section averaged slab model to predict idealized releases of dense gas. Havens (1986) also reported on the performance of the most sophisticated finite-difference and finite-element codes available. Even the most elaborate codes can make excessive numerical-diffusion errors. Only one or two of the most complex models attempt to consider terrain or heat transfer effects. Meroney (1986) compared fluid- and numerical- model predictions of Burro Spill Tests 8 and 9. They produced comparable predictions of the cloud concentration patterns.

Substances which only produce noxious odors are considered to be non-criteria pollutants by the U.S. Environmental Protection Agency since no direct physiological harm can be found due to the odors themselves. Nonetheless, odors can be a mental irritant and one can develop symptoms, such as nausea, headache, irrational behavior, and loss of appetite, caused by the shear unpleasantness of the odor. In addition, since the perceived intensity of an odor decreases less sharply than the absolute concentration, odor control often requires the largest ventilation rates and dominates equipment choice even over threshold toxic levels!

Odorants, flammable gases and toxic gases all interact with life forms over short time intervals; thus, they involve similar transport and mixing characteristics. Models proposed by Meroney (1984) or Wilson (1982) concerning the statistical character of plumes released from fume-hood exhausts or short-stacks on building roofs are equally useful for each source gas. Unfortunately, statistical models for the intermittent behavior of plumes are based on very limited data taken with instruments of limited time and spatial resolution.

Future improvements in the prediction of the consequences of hazardous gas cloud release will be depend upon advances made in several key areas. These areas include:

™ systematic field and laboratory studies of the internal character of gas clouds, the correlation of gas cloud concentration with eddy size, and the connectivity of regions exceeding LFL levels within gas clouds

™ improved understanding of the physics of the mixing process across stratified shear layers, which results in improved turbulence models to include in numerical programs

™ improvement in the understanding of near-source dilution mechanisms such as the interaction of supersonic decompression with source geometry, water and steam spray curtains, and the influence of two-phase or reactive gases.

™ improvement in the manner in which terrain effects are incorporated into numerical models, and validation of these models.

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SEMINAR/WORKSHOP ON WIND ENGINEERING: THE PAST TO THE FUTURE

DATE: 4 June 1987 **TIME:** 3:45 PM
LOCATION: Natural Resources Rm 113
Colorado State University
Fort Collins, Colorado

PAPER TITLE FOR SESSION IV: Wind Transport of Odors and Hazardous Materials

SLIDE 1: TITLE SLIDE
The objective of this paper is to review the state of fluid modeling concepts about the atmospheric transport of gases or materials which are objectionable or hazardous to the public. The presentation will emphasize gases which are problems over short time scales as opposed to air pollutants assumed to cause long-term health, corrosion or environmental deterioration. Such situations include noxious or odorous compounds, flammable gases, asphyxiants, and toxic chemicals. In the process I will identify and prioritize some research problems of importance to industry and the government for the coming decade.

Source Materials: ODORS

SLIDE 2: ODORS IN CHEMICAL PLANTS

EPA treats odors as non-criteria pollutants. Fortunately, we can often smell toxic and hazardous materials well before they become dangerous.

SLIDE 3: ODORS CAN BE NOXIOUS

Offensive odor complaints comprise the majority of air pollution complaints each year, yet their abatement is the most difficult to control and regulate.

SLIDE 4: HUMAN HEAD CROSS-SECTION

There are two chemosenstitive systems in the nose:
The olafactory bulb or olifactory epithelium
The trigeminial cranial nerves

SLIDE 5: NASAL CAVITY

The trigeminial cranial nerves distritubeted through nasal mucosa. Feelings of irritation, tickling and burning noted.

SLIDE 6: "NOSE BRAIN" or OLAFACTORY BULB

Tip area is usually about size of dime with up to 5×10^6 nerve cells

SLIDE 7: OLAFACTORY EPITHELIUM

Area appears to contain cilia buried in mucous connected to nerve cells
Similar area in dog about size of handkerchief

SLIDE 8: LOCK AND KEY CONCEPT

Chemical mechanism - shapes interfit available sites; hence, similar shape chemicals produce similar smells

SLIDE 9: TUNNING FORK CONCEPT

Physical mechanism - sympathetic vibrational states of molecules cause cilia vibration

SLIDE 10: SIGMA CURVE RESPONSE
SLIDE 11: THREHSHOLD CONCENTRATIONS

Note trimethylamine at 0.2 ppb!

SLIDE 12: ODOR SOURCES

Source materials: TOXICITY, FIRE AND EXPLOSIONS

SLIDE 1: LOUISIANA TRAIN WRECK early 1980s

Multiple material release, often in unknown configurations or combinations

SLIDE 2: LNG EXPLOSION

1944 explosion of Clevland Lighting and Illuminating Company caused 12 million dollars damage and killed 40 people.

SLIDE 3: POTENTIAL AT BROOKLYN UNION GAS COMPANY

Example of an unlikely catastrophic spill impact area

SLIDE 4: BUCKLEY AND WIENER DATA

15,000 hazardous material spills were examined for period in early 1970's. The top of the slide indicates the most frequently recorded spills. Note that sulphuric acid rates as the chemical produced in greatest quantity in the USA. The authors ranked relative hazard from 1 to 5 based on LD_{50} and hazard potential from 1 to 10 based on relative hazard and quantity of material spilled. 9 means unknown. The bottom of the slide indicates the materials with the highest mean hazard potential.

SLIDE 5: PRIMARY CAUSES AND OPERATIONAL AREAS
SLIDE 6: PRIMARY VS SECONDARY SPILL CAUSES
SLIDE 7: FREQUENCY OF SPILLS BY AREA

Source Configurations:

SLIDE 1: BOB-TAIL LPG TRAILER
SLIDE 2: LARGE CHEMICAL TRAILER
SLIDE 3: LPG OR LNG RAIL TANKER
SLIDE 4: LNG SHIP
SLIDE 5: PROCESS AREA BADAK INDONESIA
SLIDE 6: STORAGE AREA BADAK INDONESIA

SLIDE 7: SPILL CATAGORIES - F.P. Lee (1980)

Spills can be catagorized by a) fluid, b) type of plant, c) aperture, d) enclosure, e) height of release, and f) momentum of release. None of the models proposed to handle these situations have really been validated.

State of the Art: NEUTRAL PLUME PHYSICS

SLIDE 1: RESEARCH
SLIDE 2: ELEVATED PLUME - Schematic
SLIDE 3: ELEVATED PLUME - Wind tunnel
SLIDE 4: SHORT STACK - Schematic
SLIDE 5: SHORT STACK - Wind tunnel
SLIDE 6: FLUSH VENT - Schematic
SLIDE 7: FLUSH VENT - Wind tunnel

Wind tunnel studies have led to a greater understanding of the complexity of flow around obstacles. But only the simplest obstacles have been given much attention.

Recently both mean and fluctuating concentrations have been made around such obstacles by researchers in Europe, Canada and the US. Castro + Robins Wilson etc.

SLIDE 8: LI and MERONEY, 0° orrientation
SLIDE 9: 22.5° orrientation
SLIDE 10: 45° orrientation

SLIDE 11: MINIMUM DILUTION CURVES

SLIDE 12: CONCENTRATION INTENSITY vs STRING DISTANCE

SLIDE 13: CONCENTRATION STATISTICS

SLIDE 14: PREDICTION OF OFFENSIVE ODOR INCIDENCE

<u>State of the Art: DENSE PLUME PHYSICS</u>

SLIDE 1: CRYOGENIC FLUIDS

SLIDE 2: PORTON DOWNS 40 M^3 SPILLS vs WT by HALL

SLIDE 3: NUMERICAL MODELS OF SLAB AND 3D TYPES
SLIDE 4: ISO, CO_2, LIQUID N_2
SLIDE 5: ISO, LIQUID N_2, CH_4

SLIDE 6: VALIDATION EXERCISES

List of field/laboratory experiments. Continuous and instantaneous studies.

SLIDE 7: PATTERN TEST CONCEPT

Proposed by Lewellen and Sykes (1985), compares over increments of decreasing spatial resolution. Essentailly it estimates how much the predicted pattern must be shifted in space to cover all of the observed values.

SLIDE 8: BURRO MODEL TESTS AT CSU
SLIDE 9: BURRO MODEL TESTS AT CSU
SLIDE 10: BURRO 9, LAB 1:85
SLIDE 11: BURRO 9, FEM-3
SLIDE 12: BURRO 8, LAB 1:85, SG = 4.17
SLIDE 13: BURRO 8, FEM-3
SLIDE 14: SUMMARY THETA VS EXPERIMENT

It appears both laboratory and numerical can predict plumes within a spatial shift of about 12 to 15° exactly.

SLIDE 15: BMT THORNEY ISLAND TEST SERIES - Reynolds number effects
SLIDE 16: BMT PE/RI NUMBER EFFECTS - Instantaneous spills
SLIDE 17: SHELL RESEARCH/CSU PE/RI NUMBER EFFECTS - Continuous spills
SLIDE 18: PERFORMANCE ENVELOPES - SG = 1.5
SLIDE 19: PERFORMANCE ENVELOPES - SG = 4.17

<u>Mitigation Studies:</u>

SLIDE 1: BUILDINGS
SLIDE 2: VAPOR BARRIERS AND VORTEX GENERATORS
SLIDE 3: EXPT

SLIDE 4: WATER SPRAY CURTAINS

Researach Problems:

SLIDE 1: CHOICES
SLIDE 2: STATUE OF LIBERTY
SLIDE 3: LIST OF TOPICS
SLIDE 4: THE END

Hazard Potential Probability

Material	10x9 Lbs/Yr	Rank	RH	HP
Most Frequently Spilled				
Sulphuric acid	79.4	1	9	2.31
Ammon nitrate	14.0	14	9	--
Hydrochl acid	5.7	25	3	2.55
Caustic soda	5.72	7	3	2.86
Ethyl parathion	--	--	5	2.46
Highest Mean Hazard Potential				
Anhydr ammonia	32.4	3	3	6
Toulene	5.3	27	4	5.9
Nitric acid	16.1	11	4	4.7
Phenol	2.9	34	4	4.5
Methanol	8.3	18	2	3.6
Xylene	6.1	22	2	3.4

Hazard Potential Probability

Primary Spill Causes:	Hazard Potential Probability High (HP>6)	Low (HP<6)
Tank rupture or puncture	23%	77%
Tank overflow, leakage	19%	81%
Hose, transfer failure	8%	92%
Non-tank rupture (cans, drums, bottles)	3%	97%
Operational Areas:		
In plant storage	27%	73%
In plant processing	22%	78%
In transit	12%	88%
Loading or unloading	9%	91%

Primary versus Secondary Causes:

Tank rupture or puncture	54.7% Derailment, collision or rollover 33.4% Container failure 15.5% Sharp objects
Tank overflow or leakage	20.6% Personnel error 18.5% Mechanical failure 26.4% Unknown
Hose, transfer failure	75.0% Hose or coupling failure
Non-tank rupture (cans, drums, bottles)	31.1% Sharp object 25.4% Improper loading

Frequency of Spills by Operational Areas:

Transit	57%
Loading and unloading	25%
In plant process	10%
In plant storage	7%

Field/Laboratory Validation Experiments

Test	Date	Spill Size	Model Scale	Modeling Laboratory
Continuous Releases:		cubic meters/sec		
AGA LNG	1974	40	106	CSU
Avocet LNG	1978	13–20	85	CSU
Burro LNG	1980	44–70	240 85	CSU
Maplin Propane	1980	9–11	110 120	Shell Res
HSE CO2	1981	0.4	29	CSU
Thorney Island Phase III Freon/Air	1982–1984	3–5.8	40 100 150 250	BM Tech
Instantaneous Releases:		cubic meters		
Porton Freon/Air	1981	40	25	Warren Sp
Thorney Island Phase I & 2 Freon/Air	1982–1984	1400–2100	40 90 100 107 150 164	BM Tech Warren Sp BM Tech TNO BM Tech U. Hamburg

Field/Laboratory Validation Experiments

Test	Date	Spill Size	Model Scale	Pattern Intercept
Continuous Releases:		cubic meters/sec		
AGA LNG	1974	40	106	10
Avocet LNG	1978	13–	85	12.5–20
		20		
Burro LNG	1980	44–	240	15–20
		70	85	
Maplin Propane	1980	9–	110	--
		11	120	
HSE CO2	1981	0.4	29	12.5
Thorney Island	1982–	3–	40	--
Phase III	1984	5.8	100	
Freon/Air			150	
			250	
Instantaneous Releases:		cubic meters		
Porton	1981	40	25	--
Freon/Air				
Thorney Island	1982–	1400–	40	--
Phase I & 2	1984	2100	90	
Freon/Air			107	
			150	
			164	

Field/Laboratory Validation Experiments

Test	Date	Spill Size	Model Scale	Density Distortion
Continuous Releases:		cubic meters/sec		
AGA LNG	1974	40	106	No
Avocet LNG	1978	13–20	85	No
Burro LNG	1980	44–70	240 85	Yes & No
Maplin Propane	1980	9–11	110 120	Yes & No
HSE CO2	1981	0.4	29	No
Thorney Island Phase III Freon/Air	1982–1984	3–5.8	40 100 150 250	Yes & No
Instantaneous Releases:		cubic meters		
Porton Freon/Air	1981	40	25	No
Thorney Island Phase I & 2 Freon/Air	1982–1984	1400–2100	40 90 107 150 164	Yes & No