MSAA CONFERENCE '90

INHALATION TOXICITY OF
FLUOROPOLYMER/WOOD SMOKES IN FUUSCALE FIRES

R Valentine, BB Baker, JK Bonesteel, JG DiPinto, DJ Kasprzak, GT Makovec, WC Seidel, FB Clarke, H van Kuijk, CH Herpol and M Janssenns.

As shown in Figure 1, numerous people both within **DuPont,** the consulting firm of **Benjamin/Clarke** Associates, and the State University of Ghent were involved in these full-scale studies.

Our rationale for conducting full-scale fire studies with perfluoropolymers were based on several factors. The first reason, as shown in Figure 2, relates to the interest shown by both regulators and researchers on small-scale combustion toxicity test systems. The second relates to the observation that when certain perfluorinated polymers are burned in some small-scale combustion toxicity test systems, unusually toxic decomposition products may be formed. Lastly, small-scale combustion toxicity test systems are limited by the inability to recreate the ventilation, fuel load, and heat transfer characteristics which exist in real fire and therefore small-scale toxicity data may not be predictive at full-scale.

Full-scale fire studies were initiated with two objectives in mind. These objectives are shown in Figure 3. First, does the combustion of perfluorinated polymers in a large fire create smokes with an unusually toxic atmosphere, that is smoke with a potency comparable to that achieved in some small-scale test systems? Secondly, since the experimental conditions are critical to the toxic potency of materials in small-scale systems, is the smoke toxicity of perfluorinated polymers dependent upon the fire scenario?

Several important features in our experimental approach are shown in Figure 4. The first step was to define a fire scenario. We started a large fire involving a perfluoropolymer (Teflon@ **FEP/PFA** plenum cable) and evaluated the smoke toxicity at a location remote from the burn room. The fire model involved a 40 m^3 room and fuel energetically equivalent to a 1-2 megawatt fire. This equated to 100-300 kg of wood; an amount of fuel expected to produce a sustained fire hot enough to **decompost** all of the polymer.

A smoke transport system was built to cool and dilute the intensely hot smoke, and deliver it to a series of animal chambers with minimal losses.

To evaluate the smoke toxicity, groups of 10 male **Crl:CD** rates were exposed head-only to the smoke for a 30-minute period, beginning from the time the fire was started. Four preselected rats were killed immediately after exposure for carboxyhemoglobin[2] determination and pathologic examination.

An analytical scheme was devised to determine the types and amounts of fluoropolymer combustion products. Smoke samples were collected at 1-2 min intervals in evacuated gas bottles containing a dilute base; the aqueous phase was later analyzed for hydrolyzable fluorine species (F_{HYD}) with an F ion selective electrode. Fluorocarbon gases were monitored in the headspace by Fourier Transform Infrared Spectroscopy. Other parameters measured included carbon monoxide (CO), carbon dioxide (CO_2), oxygen and temperature.

Finally, a series of rangefinding tests would be conducted both with and without cable to determine the relative toxicity of the cable. In addition, several burns were conducted to determine how changes in the fire scenario involving the fuel, location of cable within the burn room and smoke transport process affect the smoke toxicity.

Teflon@ is **DuPont's** registered trademark for its family of fluorocarbon resins, fibres, film and tubing including TFE (tetrafluoroethylene), FEP (fluorinated ethylene propylene) and PFA (perfluoroalokoxy) resins.

[2] abbreviated as **COHb**

A schematic of the burn facility is shown in Figure 5. The facility consists of 3 components; a 40 m^3 concrete burn room, 13 m u-shaped corridor and a series of animal exposure chambers. Fires were started in a wood crib located in the middle of the burn room (dotted line) directly beneath a suspended tray containing the cable. Smoke for the exposure chambers was removed in an unheated stainless steel mainfold located at the ceiling near the end of the corridor.

The smoke dilution system is shown in Figure 6. Two 100-L exposure chambers, which operated at an airflow of 100 L/min, were routinely used in these studies. All exposures were conducted using animals which were exposed head-only in wire mesh restrainers.

The next series of figures represent the results from 1 burn with wood and perfluoropolymer-coated plenum cable. Although the actual values are different, the results shown in the following figures are typical of other bums.

The typical mass losses in both the wood crib and the cable tray are shown as a function of time in Figure 7. The wood burned for about 25 minutes and the polymer began to lose weight at about 5 minutes; the insulation had completely burned by about 18 minutes.

The temperature at the cable tray within the burn room and the smoke manifold are shown in Figure 8. The temperature peaks at about 900°C after about 15 minutes. Major cable loss corresponds to a temperature range of about 400-900°C. After traversing the corridor, the smoke had cooled to about 350°C at the smoke extraction manifold.

The combustion of Teflon FEP/PFA plenum cable produced a complex mixture of both fluorocarbon and hydrolyzable fluorine species, CO and C02. The composition and concentrations of the fire gases were highly time dependent.

Figure 9 reveals the temporal pattern and concentrations of the major fluorocarbon gases found at the smoke sampling point in the corridor. Low temperature combustion products like trifluoromethane (CHF_3), hexafluoropropylene (C_3F_6), and vinylidene fluoride (VF_2) were found in the initial stages of the fire. At later stages of the fire, high temperature combustion gases like hexafluoroethane (C_2F_6) and carbon tetrafluoride (CF_4) were found. No tetrafluoroethylene (C_2F_4) was found in the fire gases.

The relative concentrations of hydrolyzable fluorine (F_{HYD}) species and the major fluorocarbon gases in the high-level chamber are shown in Figure 10. Peak concentrations of fluorocarbon gases occurred sooner and were much lower in concentration on a molar basis than the hydrolyzable fluorine species. The total amount of fluorine present in either the fluorocarbon gases or the hydrolyzable fluorine components is about the same, when the concentrations of these gases are expressed on a fluorine basis.

Figure 11 shows the temporal pattern of carbon monoxide (CO) and hydrolyzable fluorine (F_{HYD}) concentrations in the high-level chamber. after an initial lag, chamber carbon monoxide concentrations increased rapidly. Relative to the hydrolyzable fluorine species, the CO concentrations peaked sooner and were about 2 to 4-fold greater in concentration than the hydrolyzable fluorine component. Some hydrolyzable fluorine species were selectively lost within the dilution system since compared to the measured concentrations of CO, hydrolyzable fluorine concentrations in the low-level chamber were about 2 fold lower than expected.

As indicated in Figure 12, physiologic stresses such as high chamber temperature and reduced oxygen concentrations were also present during the exposures and may have

contributed to the overall toxicity. This figure indicates the typical chamber temperatures and oxygen concentrations as a function of time.

The amounts of cable added and the actual amount of Teflon **FEP/PFA** insulation that burned **during** a series of 5 rangefinding exposures are shown in Table 1. Also shown are the measured gas concentrations for CO, C02 and hydrolyzable flourine, expressed in ppm-min, the **COHb** concentrations and the observed deaths in the high-level chamber.

The same amount of wood was burned in each experiment (**i.e.,** approximately 120 kg), but the amount of CO detected in the high-level chamber caried by a factor of 2. The **dose-** response relationship between CO and animal mortality was not clear in these exposures. Blood carboxy-hemoglobin values were suggestive of CO intoxication in some but not all exposures since levels greater than about 60% have been associated with death in pure gas studies. In **contract** to CO, the dose-response relationship between hydrolyzable fluorine concentration and mortality was much clearer.

Clinical signs of toxicity were more prominent in rats as the amount of fluoropolymer increased; clinical signs included lethargy, labored breathing, gasping and nasal discharges and corneal capacity. In contrast, other than slight tachypnea, no clinical signs were found in wood smoke-exposed control rats. With the exception of lethargy and labored breathing in some rats from the low level chamber in these rangefinding studies, no deaths or clinical signs were found in rats from the low-level chamber. Most rats died during the 30-minute exposure period, however, some delayed deaths (within 1-3 days) were noted.

The results of the pathologic examinations are presented in Figure 13. Although exposed rats were also examined for gross and microscopic pathologic changes, no remarkable changes were found in any organ except the lungs. Typically, the incidence, not the severity, of pulmonary edema and hemorrhage increased with the increasing amounts of perfluoropolymer. These pulmonary lesions were considerably less severe than those found following exposure to perfluoropolymers in small-scale study were considered to be severe enough to be the primary cause of death. While no rats ever died in the low level chamber, about the same incidence of edema was found in each exposure group; hemorrhage was not present. Pulmonary edema and hemorrhage ranged from minimal to mild severity and tended to be more severe in those rats which died 1 day after exposure. After 14 days of recovery, no remarkable pathologic changes were found except mild local interstitial fibrosis was found in a total of 2 surviving rats from the high level chamber; the limited incidence of fibrosis precluded associating it to the combustion products from either wood or perfluoropolymer.

The mortality results and the measured concentrations of 2 important toxicants, CO in squares and hydrolyzable fluorine, in circle, for both the high and low level chambers from a total of 11 burns are summarized in Figure 15. Concentrations are expressed in ppm-min and are plotted on a logarithmic scale. The open figures represent the data obtained from the rangefinding burns. Two burns were conducted with wood only, one resulting in 0 deaths and the other resulting in 50% mortality. The partially darkened figures represent the data obtained under different fire scenarios. For example, the (■) and (●) figures denote the use of kerosene rather than **wood** as a fuel source. The ▣ and ▣ figures represent data obtained when the cable tray was relocated to the floor, beside the fire. Finally, when the smoke transport time was reduced by bypassing the corridor, the values denoted by ⟨■⟩ and ⟨●⟩ were obtained. Overall, these data show that regardless of the fire scenario, the **observed** mortalities fall within the same general range of gas concentrations as that observed for the rangefinding studies. The dashed lines indicate the best dose-response fit by **probit** analysis for CO and F_{HYF}, assuming these gases act independently.

An important question from this data is how does the full-scale smoke toxicity of perfluoropolymers compare with other toxicants, is it orders of magnitude more toxic than other fire gases? We can make generalisations of the overall smoke toxicity based on the available data, however, definitive interpretation of the smoke toxicity of individual fire gases is presently beyond our capability. The rats were exposed to a complex gas mixture but only the major fire gases were measured; we could not quantitatively determine how these gases and the physiologic stresses associated with high temperature and low oxygen interacted and affected mortality.

For perspective, a list of reported LC50 x time products for various pure gases is included in Figure 14. LC50's for the fluorocarbons detected range from about 150,000 for hexafluoropropylene to greater than 6,000,000 ppm-min for the others. At most, the chamber concentration of these gases in the burns was less than 5000 ppm-min. Hydrogen fluoride ranges from 40,000-60,000 ppm-min, while carbonyl flouride, which decomposes into hydrogen fluoride in water is about 22,000 ppm-min. Interestingly, for CO_2 a gas which doubles respiration at about 1,000,000 ppm in 30-min pure gas studies, the lethal value is much greater than 6,000,000 ppm. For CO, a common fire gas, LC50 values range from 90-150,000 ppm-min.

In the full-scale studies, LC50's were calculated by probit analysis for the hydrolzable fluorine species and CO; these calculations were based on data obtained from all 11 burns assuming these gases acted independently. The data suggests that the levels of hydrolyzable fluorine are within the factor of 3 and the levels of CO are within a factor of 2 for that reported with pure gases. Moreover, chemical analysis revealed that the hydrolyzable fluorine component of the fire gases was not associated with an organic component, indicating that the flouride was derived from either hydrogen fluoride or carbonyl flouride, and not from perfluoroisobutylene or other components. given the spectrum of insults these animals experienced, the similarity of these derived values to their reported lethality values strongly suggest than no unusually toxic products were involved in the deaths.

The major observations and conclusions are summarized in Figures 16 and 17. We found that the smoke represented a complex mixture of gases including CO_2, CO, fluorochemicals and hydrolyzable fluorine species. While the amounts of CO and hydrolyzable fluorine species were present in toxicologically significant amounts, both gases along with high temperature, CO_2, and CO probably interacted to affect the overall mortality. Clinical signs of toxicity were consistent with exposure to an irritant like hydrogen fluoride. The number of animals exhibiting pulmonary pathology increased as the amount of cable burned increased. On the other hand, the pulmonary effects were minimal and not considered to be the primary cause of death; the pulmonary pathology was less severe than that found in perfluoropolymer combustion in small-scale studies. In some experiments, the levels of CO and COHb were either at or approached lethal levels. With respect to the fire scenario, the toxicity of perfluorinated cables was not affected by either the fuel source, the location of the cable with respect to the fire, nor the distance travelled by the smoke. Finally, the derived LC50's for hydrolzable fluorine and CO, were within a factor of 3 that reported for pure gases. In conclusion, we found no evidence for unusually toxic smokes from fluoropolymers.

FIGURE 1

Inhalation Toxicity of Fluoropolymer/ Wood Smokes in Full-Scale Fires

R. Valentine, B.B. Baker, J.K. Bonesteel, J.G. DiPinto,
D.J. Kasprzak, G.T. Makovec and W.C. Seidel
(E.I. Du Pont de Nemours and Co., Inc., Wilmington, DE)

F.B. Clarke, H. van Kuijk
(Benjamin/Clarke Associates, Kensington, MD)

C.H. Herpol, M. Janssens
(State University of Ghent, Ghent, Belgium)

FIGURE 2

Rationale for a Full-Scale Fire Study

Interest in Small-Scale Combustion Toxicity Test Systems

– Need to Understand Smoke Toxicity

– Value in Material Development and Hazard Assessment

Small-Scale Combustion Tests with Perfluoropolymers

– May Yield Unusually Toxic Combustion Products

– Identity of Toxicant is Not Known

– Results ate Method Dependent

• Relevance of Small-Scale Data to Real Fires

MSAA 1990 Proceedings

FIGURE **3**

Objectives

Does the combustion of perfluorinated Teflon®
polymers in a large fire create an unusually toxic
atmosphere?

Is the smoke toxicity from perfluorinated Teflon®
polymers dependent upon the fire scenario?

FIGURE 4

Experimental Approach

- Define a Fire Scenario
  - Teflon² FEP/PFA Plenum Cable
  - 40 M3 Room, 1-2 MW Fire (100-130 kg Wood)
- Develop Smoke Transport and Animal Exposure Systems
- Evaluate Toxicity in 10 Rats Exposed to Smoke for 30-Min.
  - Immediately Post Exposure (4 Rats) COHb, Pathology
  - 14 Days Post Exposure: Deaths, Clinical Signs, Pathology

  - F_{HYD}, Fluorocarbons, CO, CO_2, O_2, Temperature
- Conduct Series of Test Burns
  - Fuel Source, Cable Location, Smoke Transport

FIGURE 5

Burn Facility Layout

Burn Room
(3.7x4.3x2.5m)

(smoke)

Corridor
Opening

Corridor
(6.6x1.5x2.5m)

Exhaust
Hood

Sampling Point
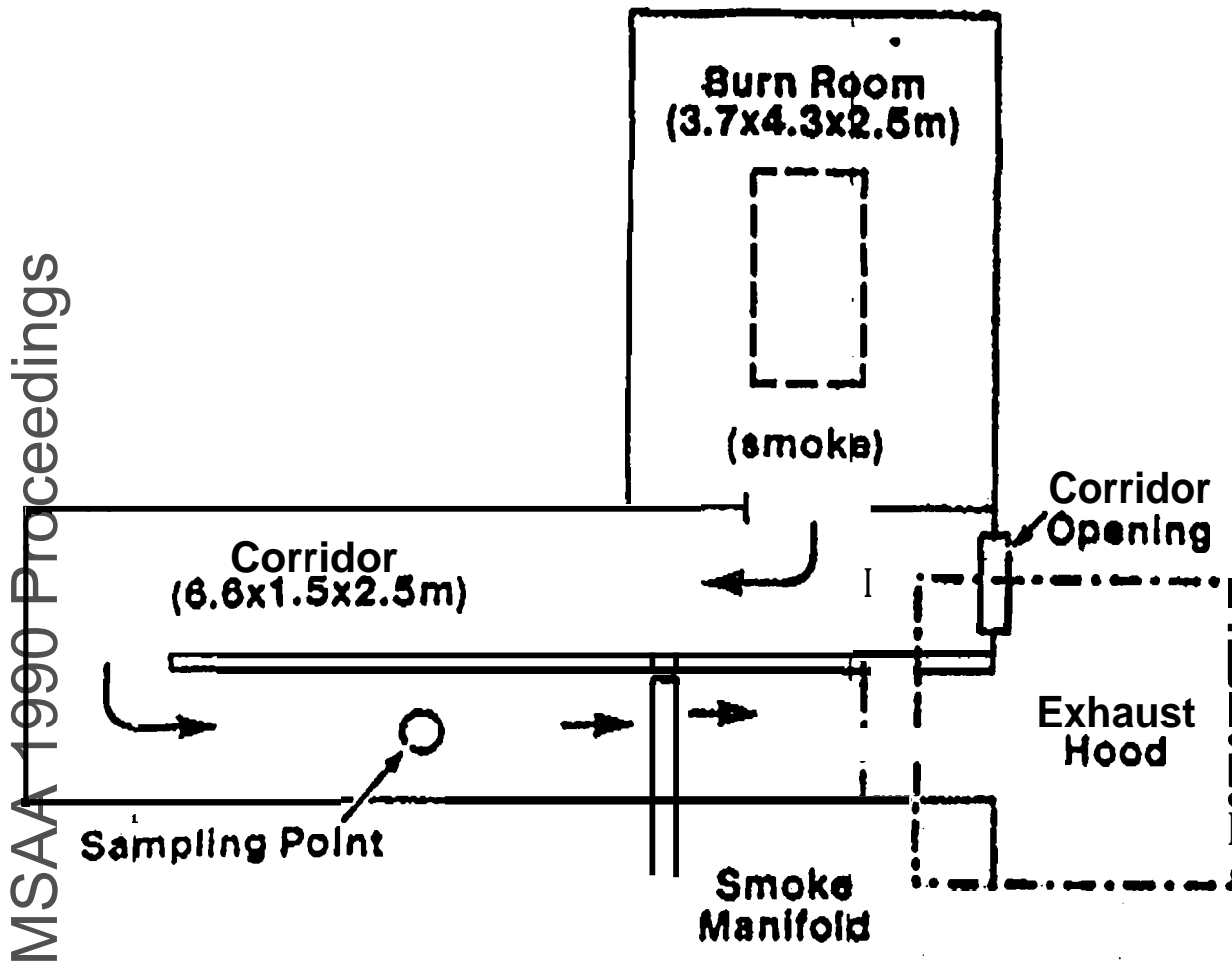
Smoke
Manifold

FIGURE 6

Smoke Dilution System
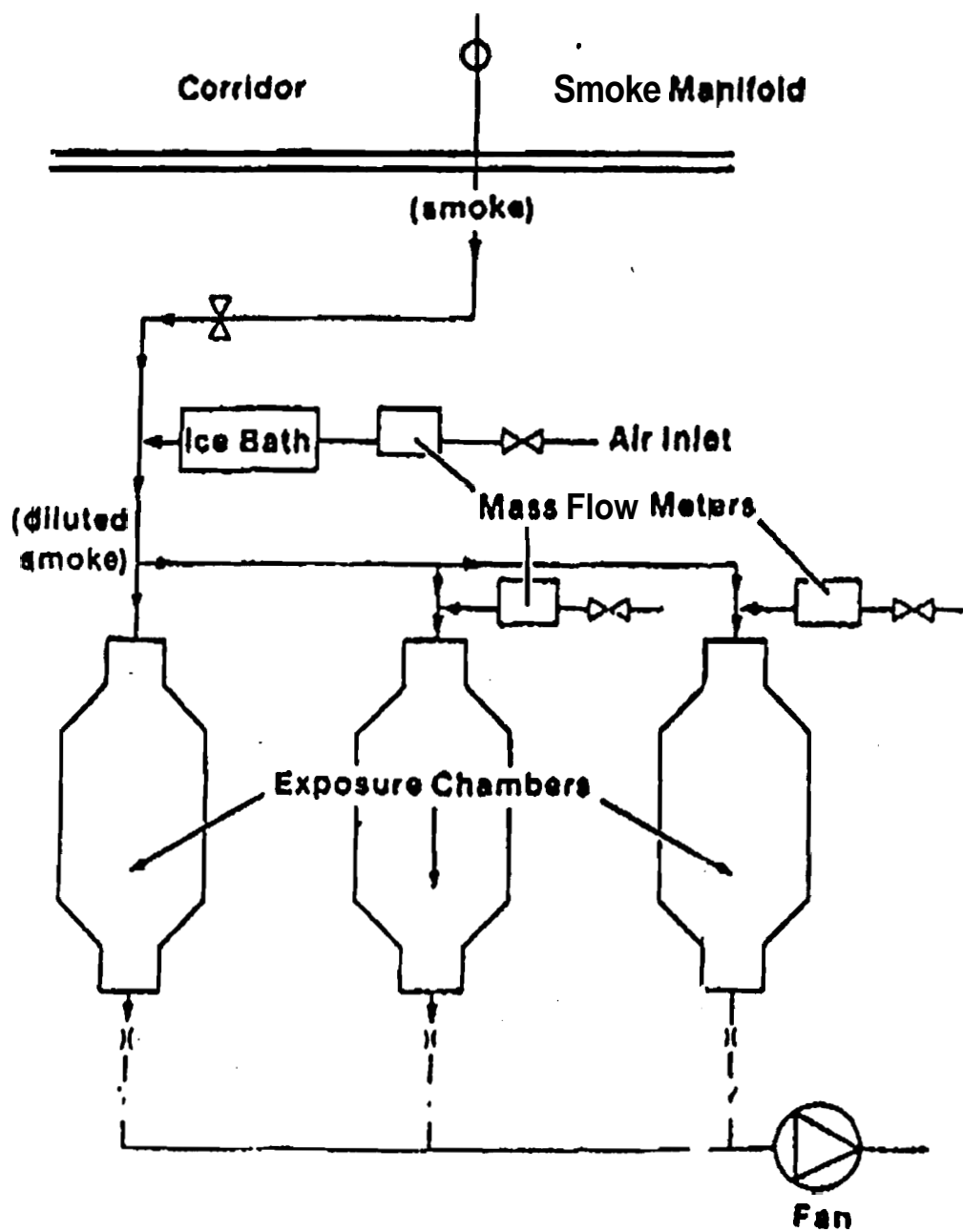
FIGURE 7

Wood and Cable Mass
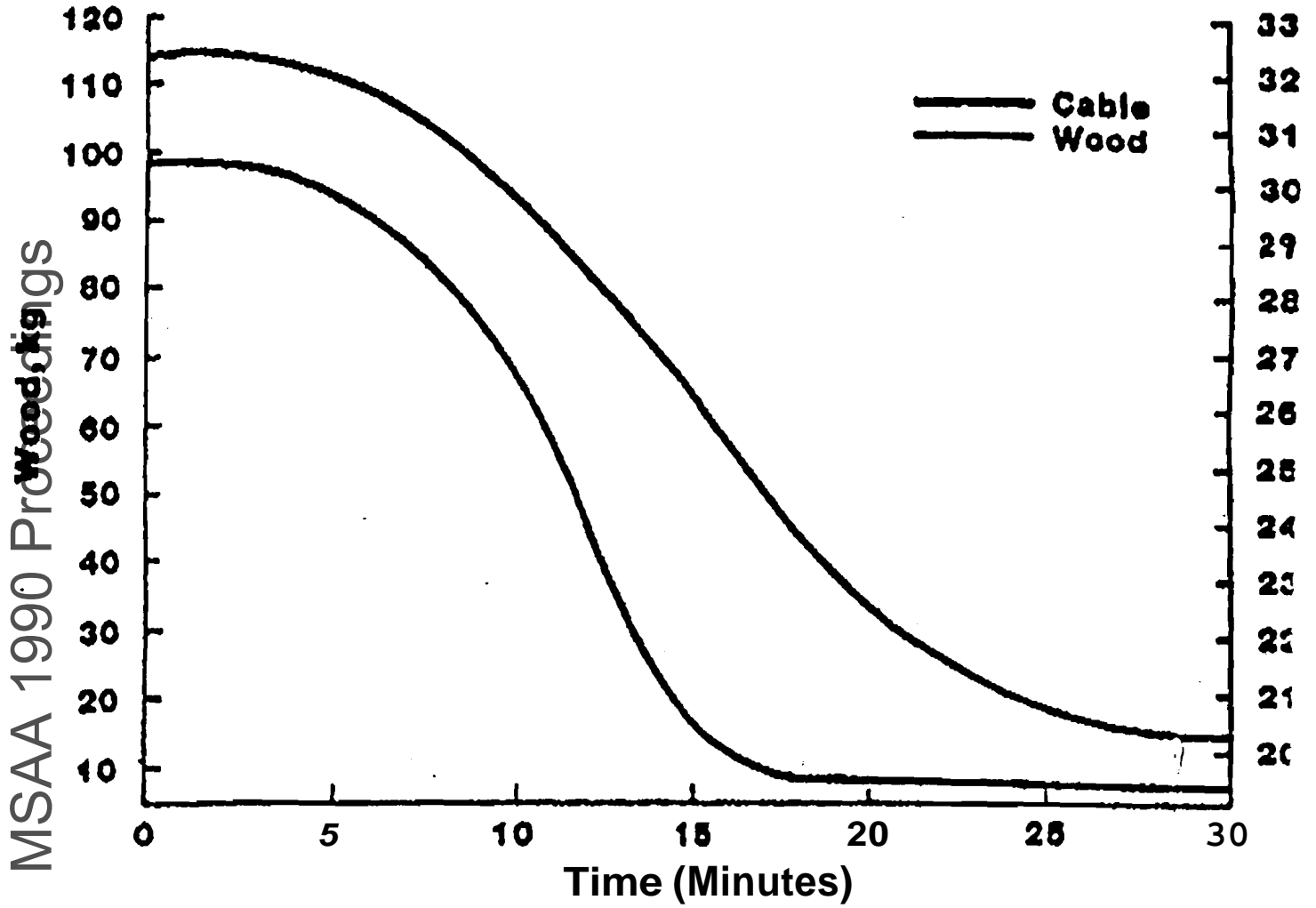
FIGURE 8

Cable Tray and Smoke Manifold Temperature
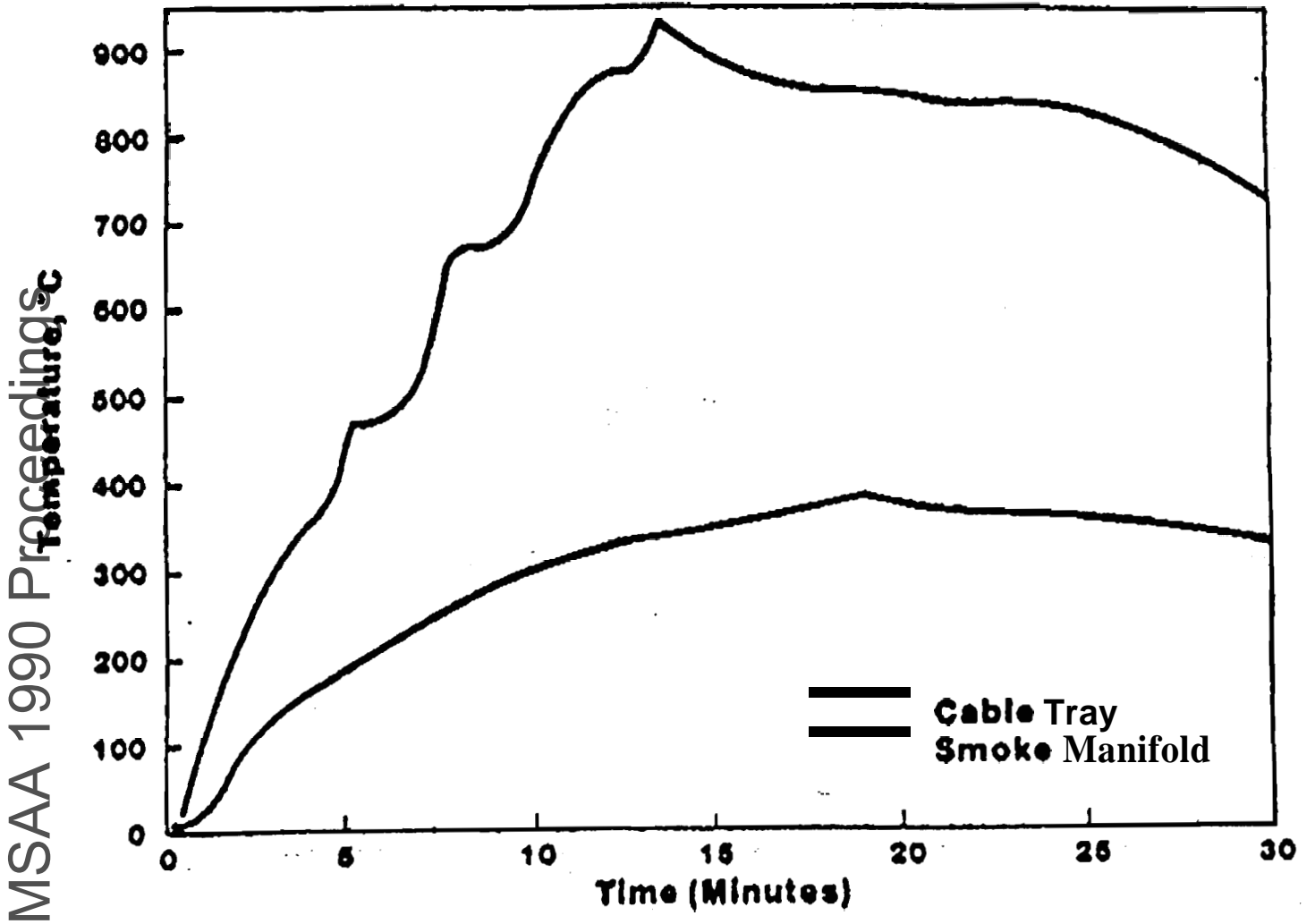
FIGURE 9

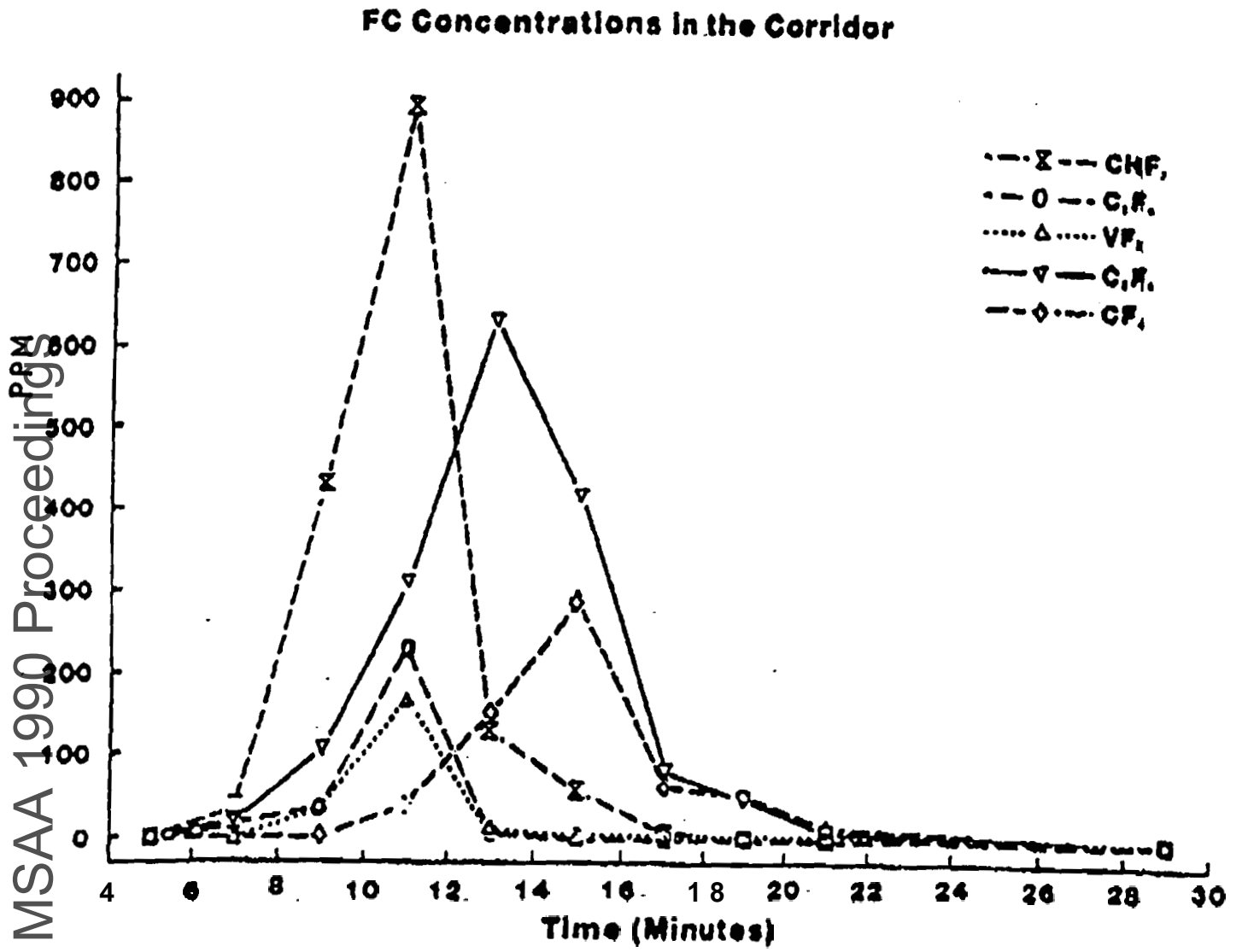## FC Concentrations in the Corridor

MSAA 1990 Proceedings

FIGURE 10

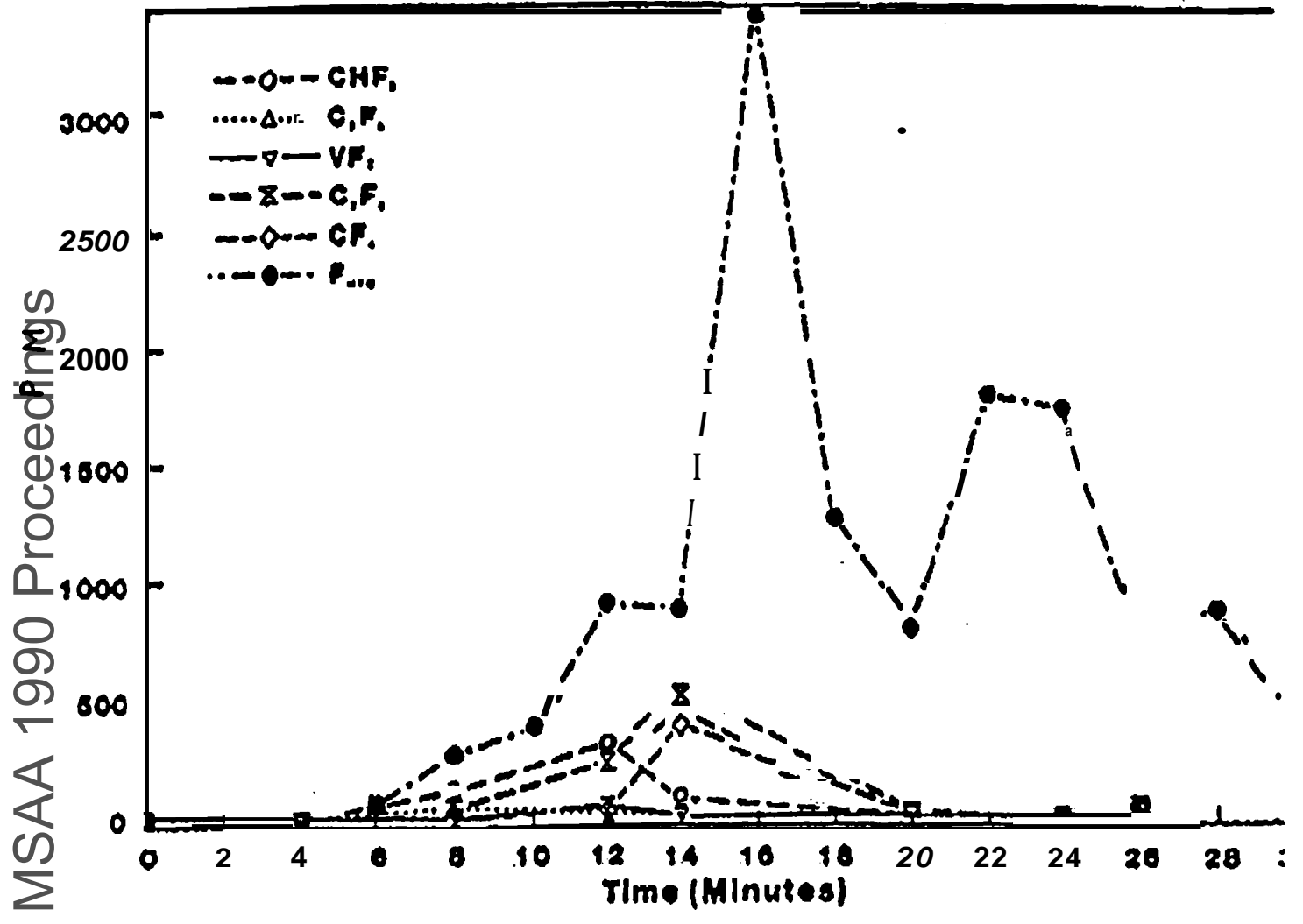FC and F... Concentrations in the High-Level Chamber

FIGURE 11
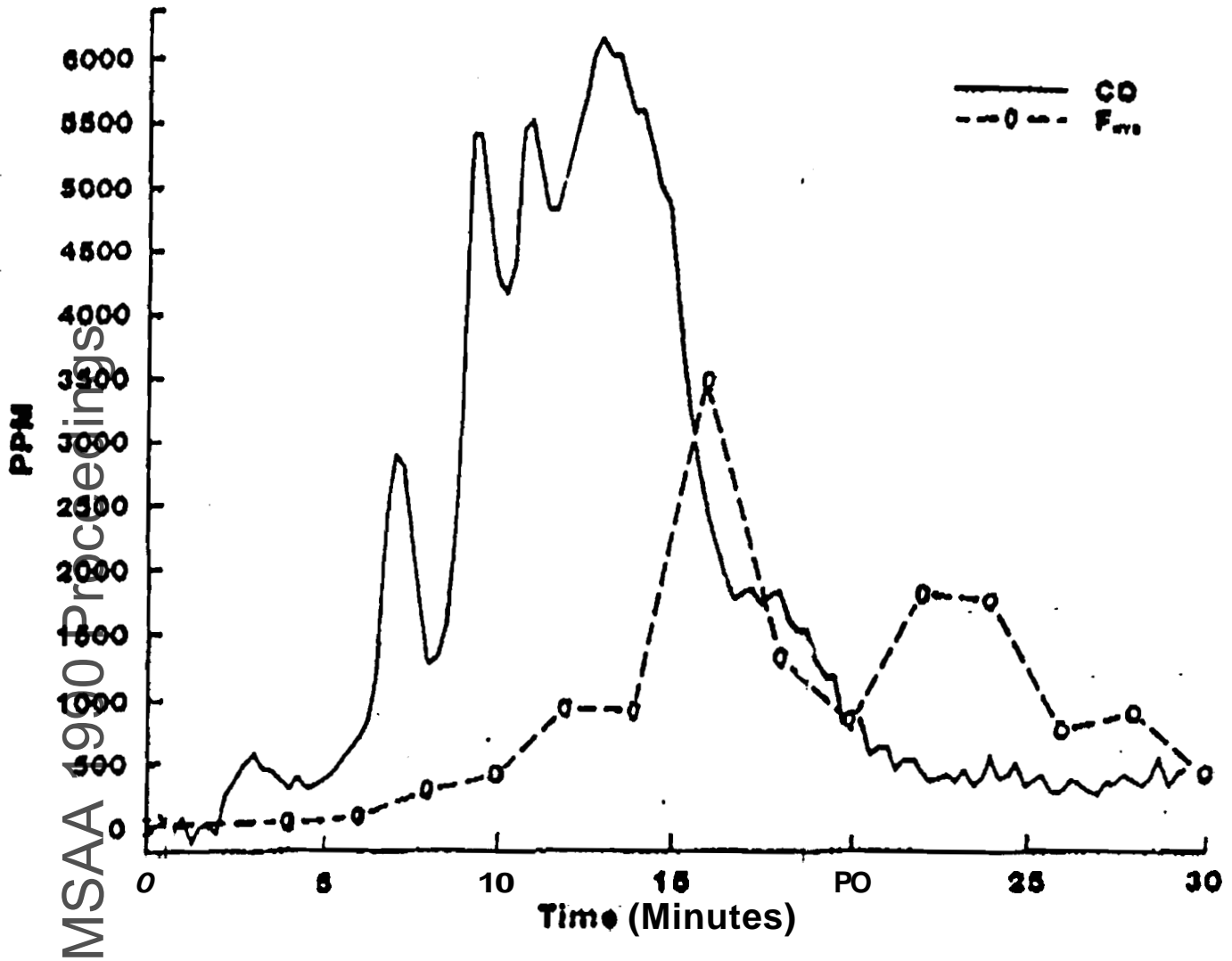

CO and F... Concentrations in the High-Level Chamber

FIGURE 12

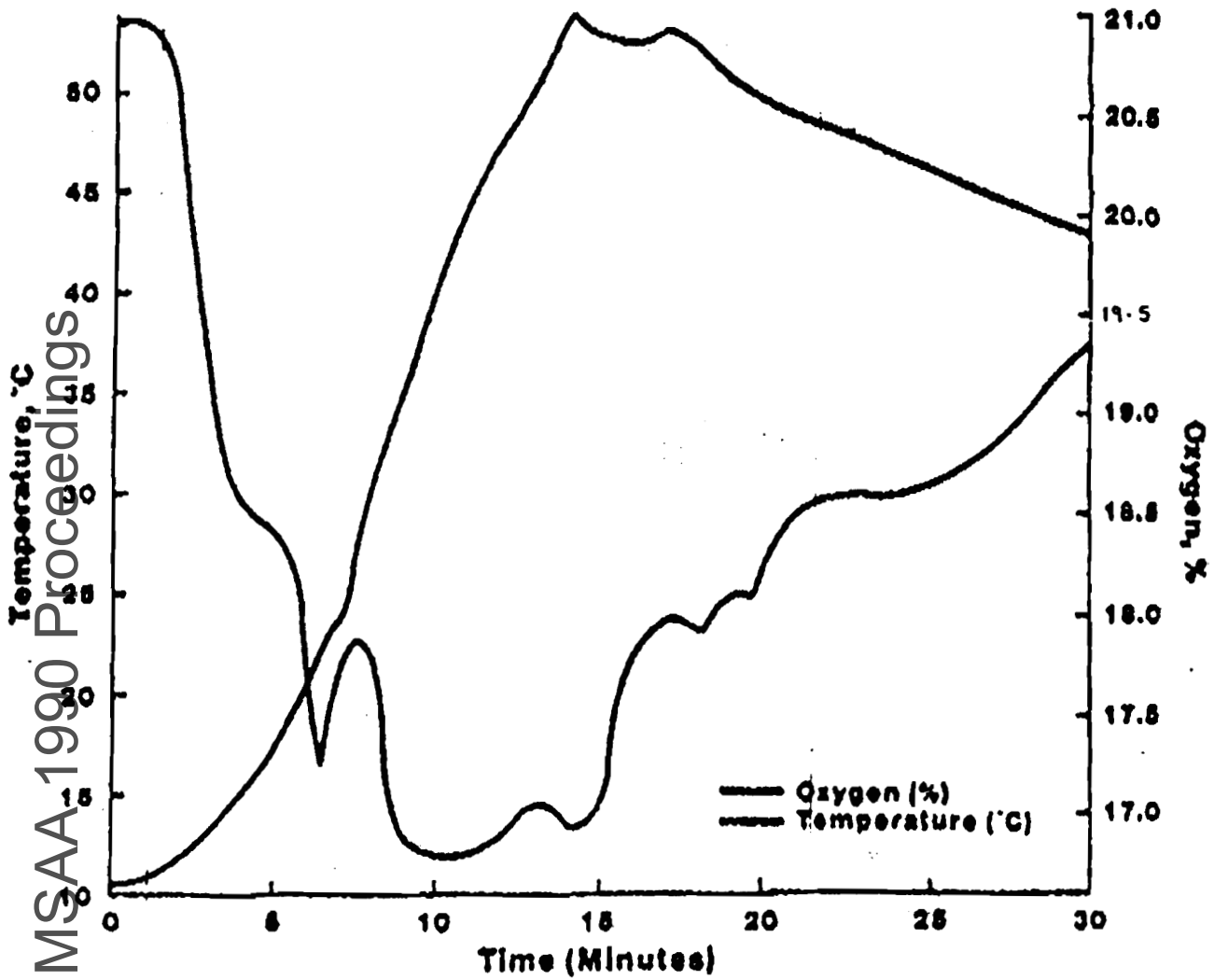O₂ Concentration and Temperature in the High-Level Chamber

TABLE I

Rangefinding Exposures

Cable Mass (kg)	0	19	25	30	30
Polymer (kg)		9	11	14	14
CO (ppm·min)	54,700	403,600	77,200	114,300	66,900
COHb (%)	52	60	64	60	54
CO_2 (ppm·min)	1,080,000	839,000	952,000	1,094,000	1,170,000
F_{HYD} (ppm·min)	—	7,000	19,200	36,600	31,600
Mortality	0/6	1/6	5/6	6/6	5/6
Delayed Deaths	—	—	3	—	2

FIGURE 13

Pathology

- Pathologic Changer Were Limited to the Lungs

- Incidence of Edema and Hemorrhage Increased with Amount of Polymer

- Pathology was Not Consistent with Effects Seen in Small Scale Studio.

- Lung Damage Not Considered to be Primary Cause of Death

- Hemorrhage Not Seen In Rats From Low-Level Chamber

- Edema and Hemorrhage Ranged from Minimal-Mild Severity
  More Severe In Rats Dying 1 Day Post Exposure

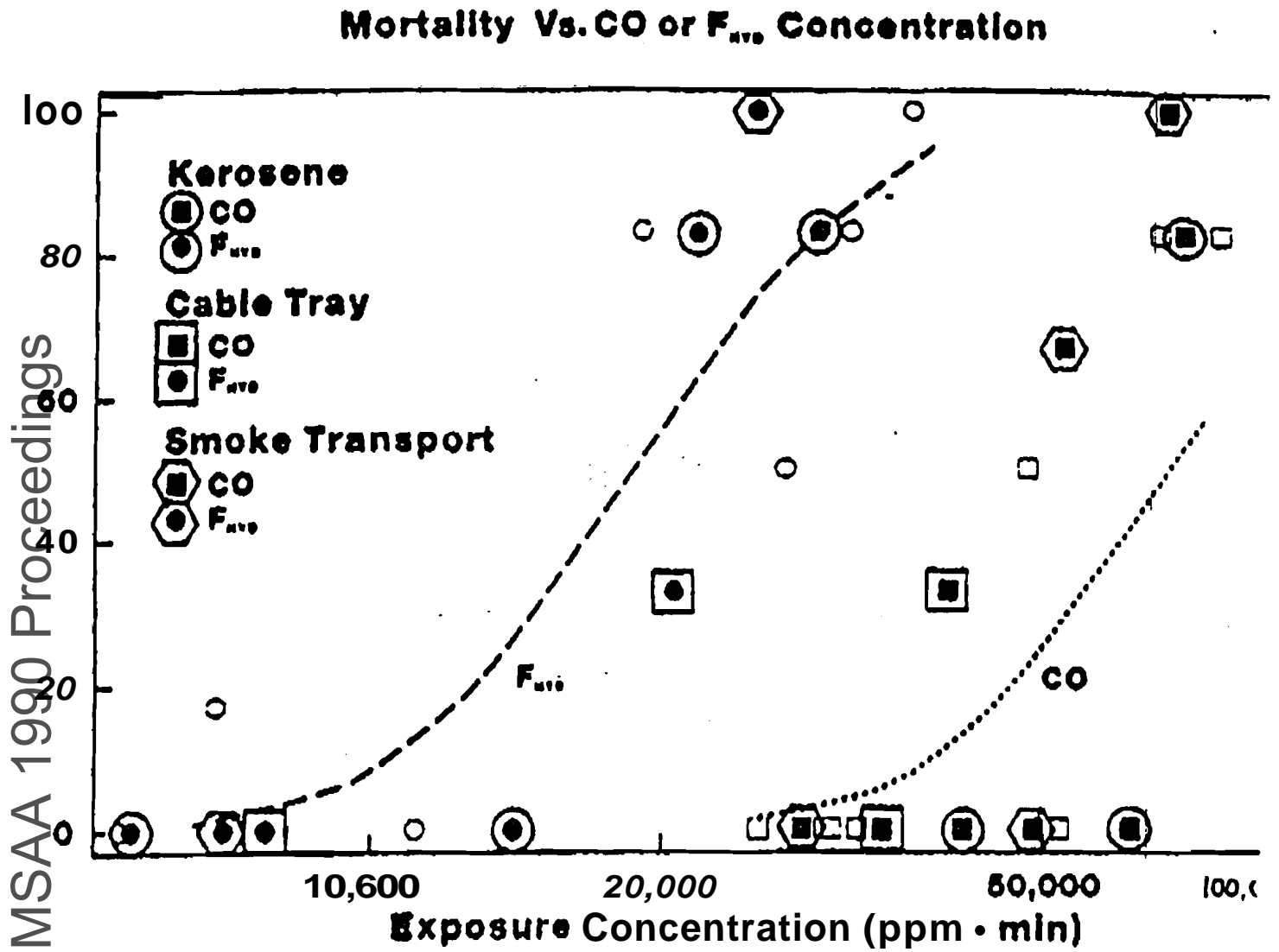- Lungs Were Normal 14 Days Post Exposure, Except Some Fibrosis in Rats From High-Level Chamber

FIGURE 14

Reported LC50 x T Products

Toxicant	LC50 x T Products (ppm-min)
CHF_3, CF_4, C_2F_6, VF_2	> 6,000,000
C_3F_6	150,000
HF	40,000–60,000
COF_2	22,000
CO_2	> 6,000,000
CO	90,000–150,000

Derived LC50 x T Products

F_{HYD}	19,000
CO	68,000

FIGURE 15

Mortality Vs. CO or F_{ave} Concentration

FIGURE 16

Observations and Conclusions

- Smoke Represents a Complex Mixture of Gases.
  - $CO_2 > CO > F_{HYD} >$ Fluorocarbon Gases

- CO and F_{HYD} Were Present in Toxicologically Important Quantities
  - Possible Interactions With Temperature, CO_2 and O_2

- Clinical Signs Consistent With HF Intoxication

  Incidence of Pulmonary Edema and Hemorrhage was Related to F_{HYD}
  - Results Went Not Consistent With Effects Seen in Small Scale Studies

FIGURE 17

Observations and Conclusions

- COHb and CO Concentrations Were Often Near Lethal Levels

- Smoke Toxicity of Perfluoropolymers was Not Affected by the Fuel Source, Location of the Cable or the Smoke Transport System

- Derived LC50's for CO and F_{HYD} are Comparable to Pure Gases

- Evidence for Unusually Toxic Smokes was Not Found at Full Scale