CHLORINATED DIOXIN AND FURAN FORMATION, CONTROL AND MONITORING

Presented at

ICCR Meeting

Research Triangle Park

September 17, 1997

Dr. Brian Gullett

EPA

(919) 541-1534

bgullett@engineer.aeerl.epa.gov

Dr. Randy Seeker

EER Corporation

(714) 859-8851

RSeeker@compuserve.com

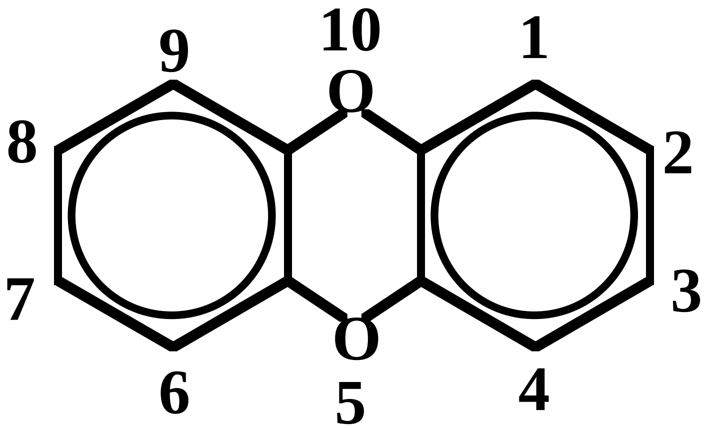
ACKNOWLEDGMENTS

- Jim Kilgroe, EPA Office of Research and Development
- Steve Lanier, EER Corporation, North Carolina
- Glenn England, EER Corporation, Irvine, CA

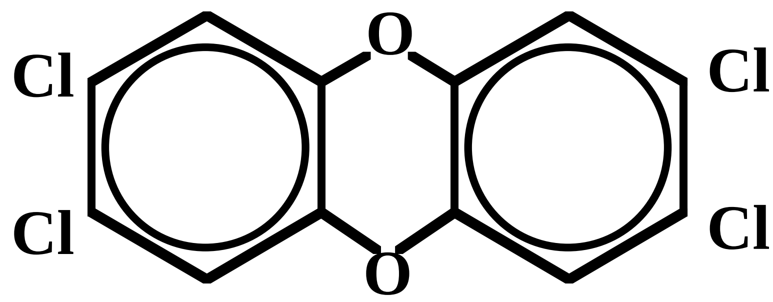
OUTLINE OF TALK

- Structures
- Concentrations of interest
- Measurement Techniques and Issues
- Fundamental Principles
- Dioxin and Furan Formation Chemistry
- Control Technologies
- Formation Conditions
- Monitoring Technologies
- Conclusions
- Recommendations

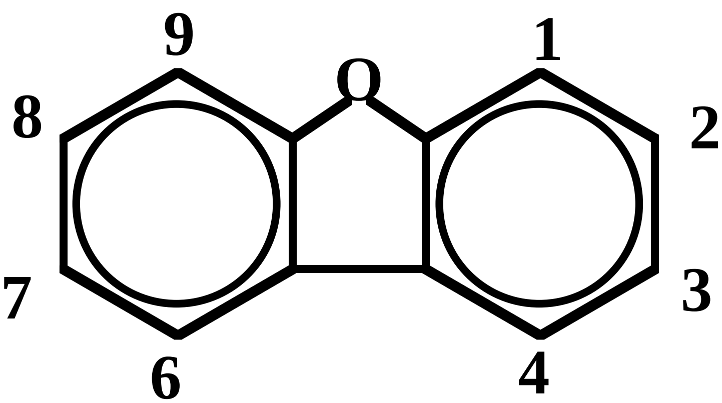
DIOXIN AND FURAN STRUCTURE



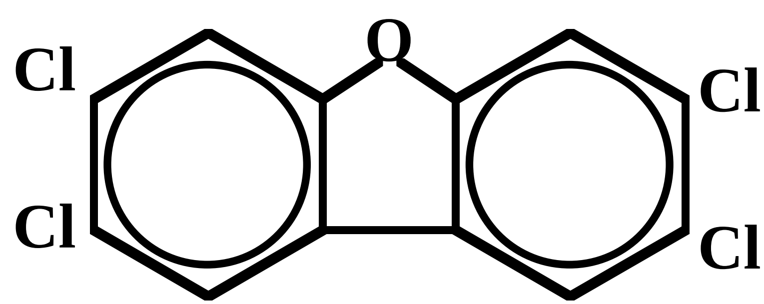
Dioxin



2,3,7,8 — Tetrachlorodibenzo(p)dioxin



Furan



2,3,7,8 — Tetrachlorodibenzofuran

- There are 210 different congener configurations.

CONGENERS TOXIC EQUIVALENT FACTOR

- 17 out of the 210 have toxic equivalency factors

Congener	NATO Toxic Equivalent Factors (I-TEQ)
2378 TCDD	1
12378 PeCDD	0.5
123478 HxCDD	0.1
123678 HxCDD	0.1
123789 HxCDD	0.1
1234678 HpCDD	0.01
OCDD	0.001
2378 TCDF	0.1
12378PeDF	0.05
23478 PeCDF	0.5
123478 HxCDF	0.1
123789 HxCDF	0.1
123678 HxCDF	0.1
234678 Hx CDF	0.1
1234678 HpCDF	0.01
1234789 HpCDF	0.01
OCDF	0.001

WORLD HEALTH ORGANIZATION (TEF)

CONGENER	TOXIC EQUIVALENCY FACTOR (TEF) HUMANS/ MAMMALS	FISH a	BIRDS a
2,3,7,8-TCDD	1	1	1
1,2,3,7,8-PeCDD	1	1	1 f
1,2,3,4,7,8-HxCDDD	0.1 a	0.5	0.05 f
1,2,3,6,7,8-HxCDD	0.1 a	0.01	0.01 f
1,2,3,7,8,9-HxCDD	0.1 a	0.01	0.1 f
1,2,3,4,6,7,8-HpCDD	0.01 a	0.001	0.1 f
OCDD	0.0001 a	-	-
2,3,7,8-TCDF	0.1	0.05	1 f
1,2,3,7,8-PeCDF	0.05	0.05	0.1 f
2,3,4,7, 8-PeCDF	0.5	0.5	1 f
1,2,3,4,7,8-HxCDF	0.1	0.1	0.1 c,f
1,2,3,6,7,9-HxCDF	0.1	0.1 c	0.1 c,f
1,2,3,7,8,9-HXCDF	0.1 a	0.1 c,e	0.1 c
2,3,4,6,7,8-HxCDF	0.1 a	0.1 c	0.1 c
1,2,3,4,6,7,8-HpCDF	0.01 a	0.01 b	0.01 b
1,2,3,4,7,8,9-HpCDF	0.01 a	0.01 b,e	0.01 b
OCDF	0.0001 a	0.0001 b,e	0.0001 b
3,4,4',5-TCB (81)	0.0001 a,b,c,e	0.0005	0.1
3,3',4,4'.TCB (77)	0.0001	0.0001	0.05
3,3',4,4',5-PeCB(126)	0.1	0.005	0.1
3,3',4,4',5,5'-I xCB (169)	0.01	0.00005	0.001
2,3,3',4,4'-PeCB(105)	0.0001	<0.000005	0.0001
2,3,4,4',5-PeCB(114)	0.0005 a,b,c,d	<0.000005 b	0.0001 g
2,3',4,4',5-PeCB(118)	0.0001	<0.000005	0.00001
2',3,4,4',5-PeCB(123)	0.0001 a,c,d	<0.000005 b	0.00001 g
2,3,3',4,4',5-HxCB (156)	0.0005 b,c	<0.000005	0.0001
2,3,3',4,4',5'-HxCB (157)	0.0005 b,c,d	<0.000005 b,c	0.0001
2,3',4,4',5,5'-HxCB (167)	0.00001 a,d	<0.000005 b	0.00001 g
2,3,3',4,4',5,5'-HpCB (189)	0.0001 a,c	<0.000005	0.00001 g

"-" indicates no TEF because of lack of data

a) limited data set

b) structural similarity

c) QSAR modelling prediction from CYP1A induction (monkey, pig, chicken, or fish)

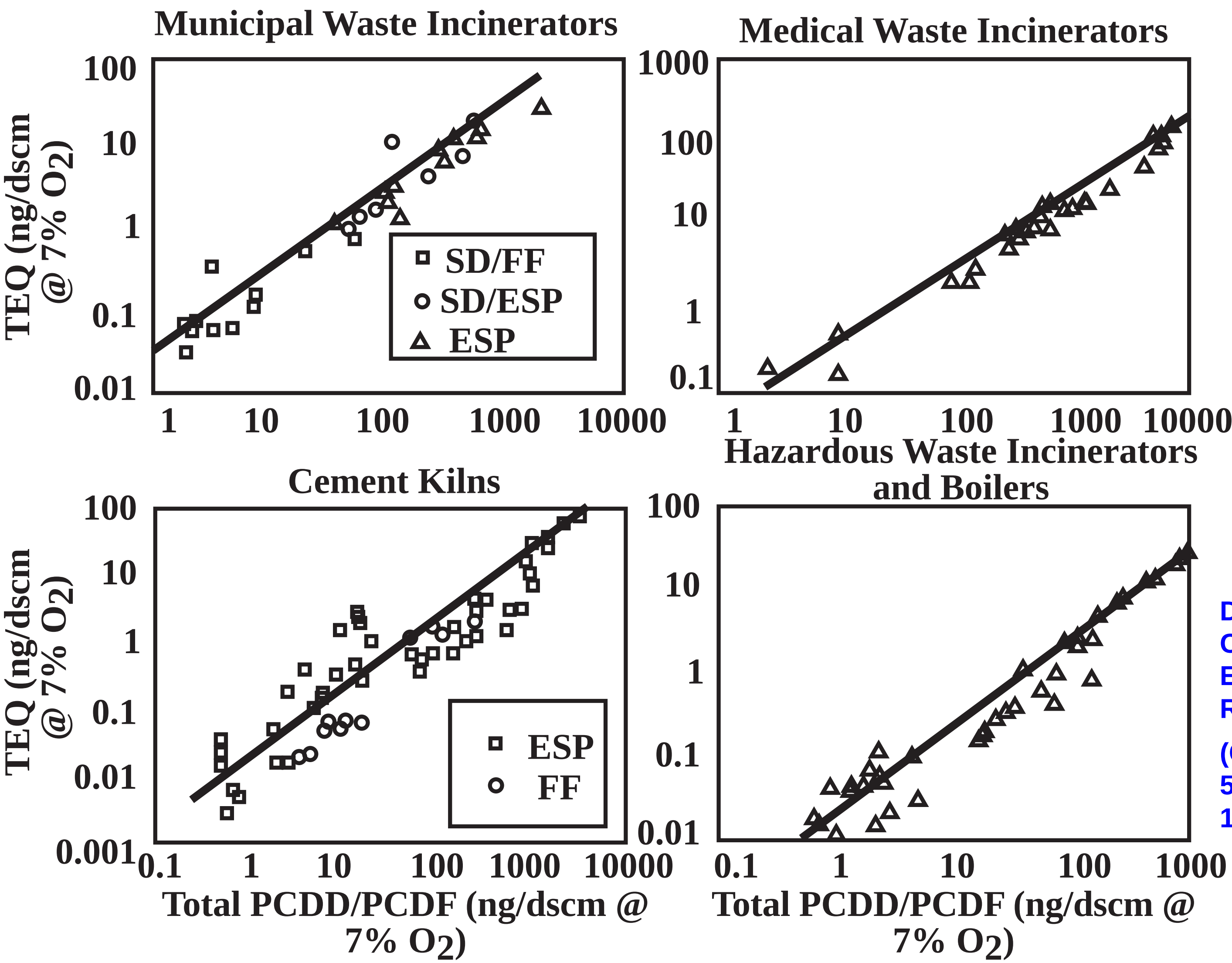
d) no new data from 1993 review

e) in vitro CYP1A induction

f) in vivo CYP1A induction after in ovo exposure

g) QSAR modelling prediction from class specific TEFs

RELATING TEQS TO TOTAL PCDD/PCDF



Data From Combustion Emissions Technical Resource Document (CETRD) EPA 530-R-94-014, May 1994

OUTLINE OF TALK

- Structures
- **Concentrations of interest**
- Measurement Techniques and Issues
- Fundamental Principles
- Dioxin and Furan Formation Chemistry
- Control Technologies
- Formation Conditions
- Monitoring Technologies
- Conclusions
- Recommendations

LEVELS OF DIOXIN OF INTEREST

- Currently levels in standards or proposed standards
  - *New Large Municipal Solid Waste Combustors*
    - 13 ng/dscm total or 0.2 TEQ (@7 % O_2)
  - *New Large (500lb/hr) Medical Waste Combustors*
    - 25 ng/dscm total or 0.6 TEQ
  - *New Large Hazardous Waste Incinerators (proposed)*
    - 0.2 ng/dscm TEQ
- What is a ng/dscm?
  - *nanogram (10^{-9} gram) per dry standard cubic meter*
  - *10 ng/dscm of PeCDD corresponds to .6 parts per trillion*
    - one person out of 100 world populations
  - *If room size of 100 x 100 x 10 ft*
    - if dioxin concentration is 1 ng/dscm there are approximately 0.000003 gm of dioxin in the room

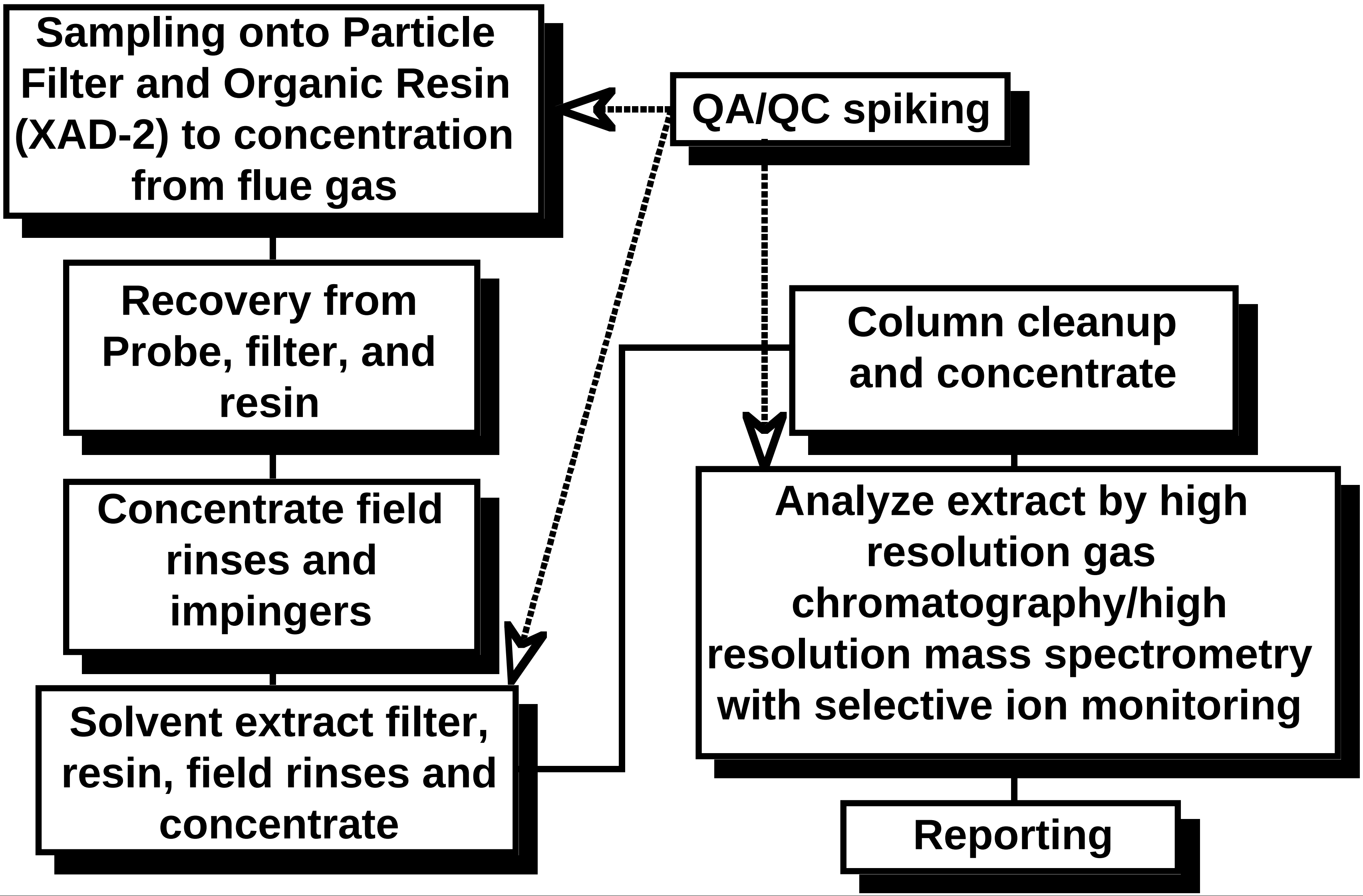
OUTLINE OF TALK

- Structures
- Concentrations of interest
- Measurement Techniques and Issues
- Fundamental Principles
- Dioxin and Furan Formation Chemistry
- Control Technologies
- Formation Conditions
- Monitoring Technologies
- Conclusions
- Recommendations

PCDD/PCDF MEASUREMENTS

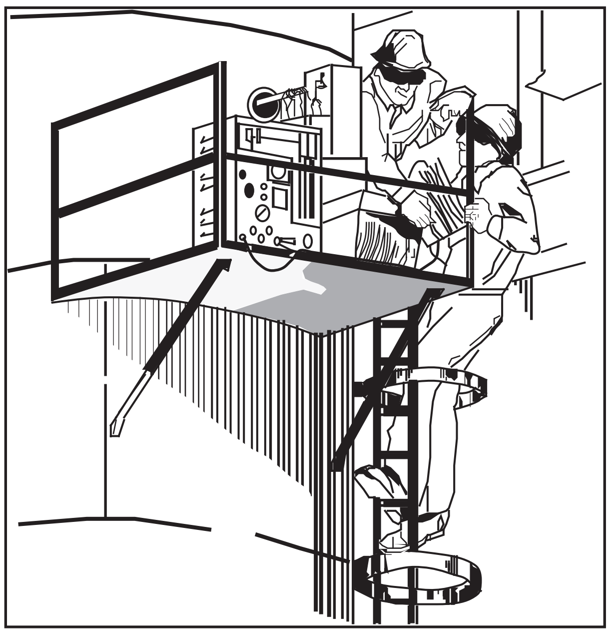
- **Manual Sampling -> Laboratory Analysis**
  - *Collect on filter & resin using Modified Method 5 train*
    - Glass probe and sample system components
  - *Complex & sophisticated laboratory analysis*
- **Cleanliness and QA/QC is essential**
- **Labor and time intensive = $$$$$**
  - *3-5 days in the field to collect samples, 3-6 weeks typical lab turnaround time*
  - *Typically 3 months from start to finish*
- **Variations in the reference methods**
  - *EPA (23, 23A, 0010/8290) , California(428) , Canada*
  - *EPA Methods can be found on Internet: http://134.67.104.12/html/emtic/cfr prom.htm*

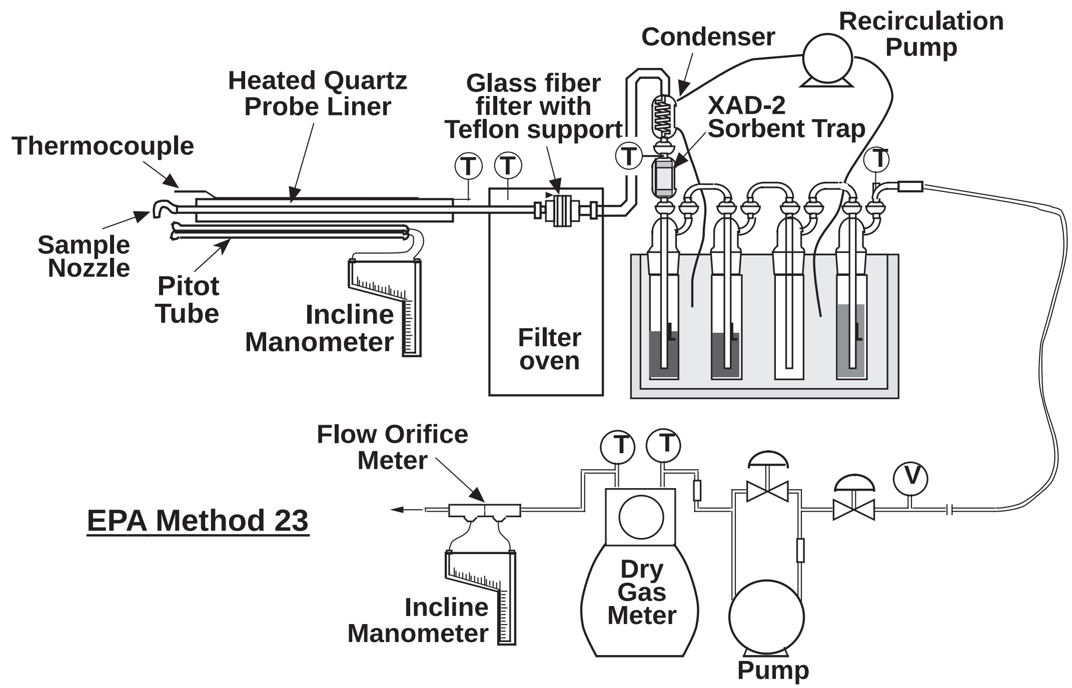
OVERVIEW MEASUREMENT TECHNIQUES



FIELD SAMPLING

Three test runs: typically three 10-12 hour days (4-6 hours sampling plus setup and sample recovery for a crew of 3-4)





- ❑ QA/QC samples (field train blanks, field reagent blanks)
- ❑ Typically 4 to 5 complete samples, 4-6 field fractions each -> 16-30 samples shipped to the laboratory

REPORTING OF DIOXIN DATA

- Treatment of detection limits
  - *zero, half detection, or at detection limit*
- TEQ treatment
  - *selection of TEF protocol*
- Measurement technique
  - *details of sampling and analysis procedures can significantly influence the results*
  - *can make data comparisons difficult*
- Emissions Concentrations
  - *Percent Oxygen (7% in U.S. vs. 11% in Europe)*
    - **Rule of Thumb: Multiply European Data by 1.404 to compare with North American Data**
  - *Different Rounding Procedures*
- Reporting and treatment of blank and recovery results

MEASUREMENT LIMITS

- Field data often have large variability
  - *Rule of thumb: PCDD/PCDF data has ± factor of two variability*
- Controlled emission concentrations data frequently below field blanks
- Sources of Variability
  - *Process Variations*
  - *Sampling Variations*
    - Sampling Conditions Variability
    - Field sampling team
    - Sample recovery
  - *Analytical Variations*
    - extraction and spike recovery
    - matrix effects
    - hysteresis effects

PRACTICAL LIMIT OF QUANTITATION (PLQ'S)

Definitions

- *"PLQ is the lowest level above which quantitative results may be obtained with an acceptable degree of confidence"*
  - **Federal Register, V57, No. 250, December 29, 1992.**
- *EPA Method 301- " The PLQ is defined as 10 times the standard deviation, at the blank level. This corresponds to an uncertainty of ±30 percent at the 99-percent confidence level"*
  - **analytical process variability**
  - **does not address accuracy and precision from source variation, field sampling and site specific matrix effects.**

PRACTICAL LIMIT OF QUANTITATION (PLQ'S)

- Significant controversy over how a PLQ should be defined for trace species
  - *What level can be routinely be measured with defined accuracy?*
  - *What standard can be enforced with the currently available sampling and analysis procedures?*
  - *Some studies have indicated that sampling and analytical variations are significant for PCDD/PCDF and that PLQ can be higher than established standards.*
  - *Method 23 data are not corrected for spike recovery or blank levels*

OUTLINE OF TALK

- Structures
- Concentrations of interest
- Measurement Techniques and Issues
- **Fundamental Principles**
- Dioxin and Furan Formation Chemistry
- Control Technologies
- Formation Conditions
- Monitoring Technologies
- Conclusions
- Recommendations

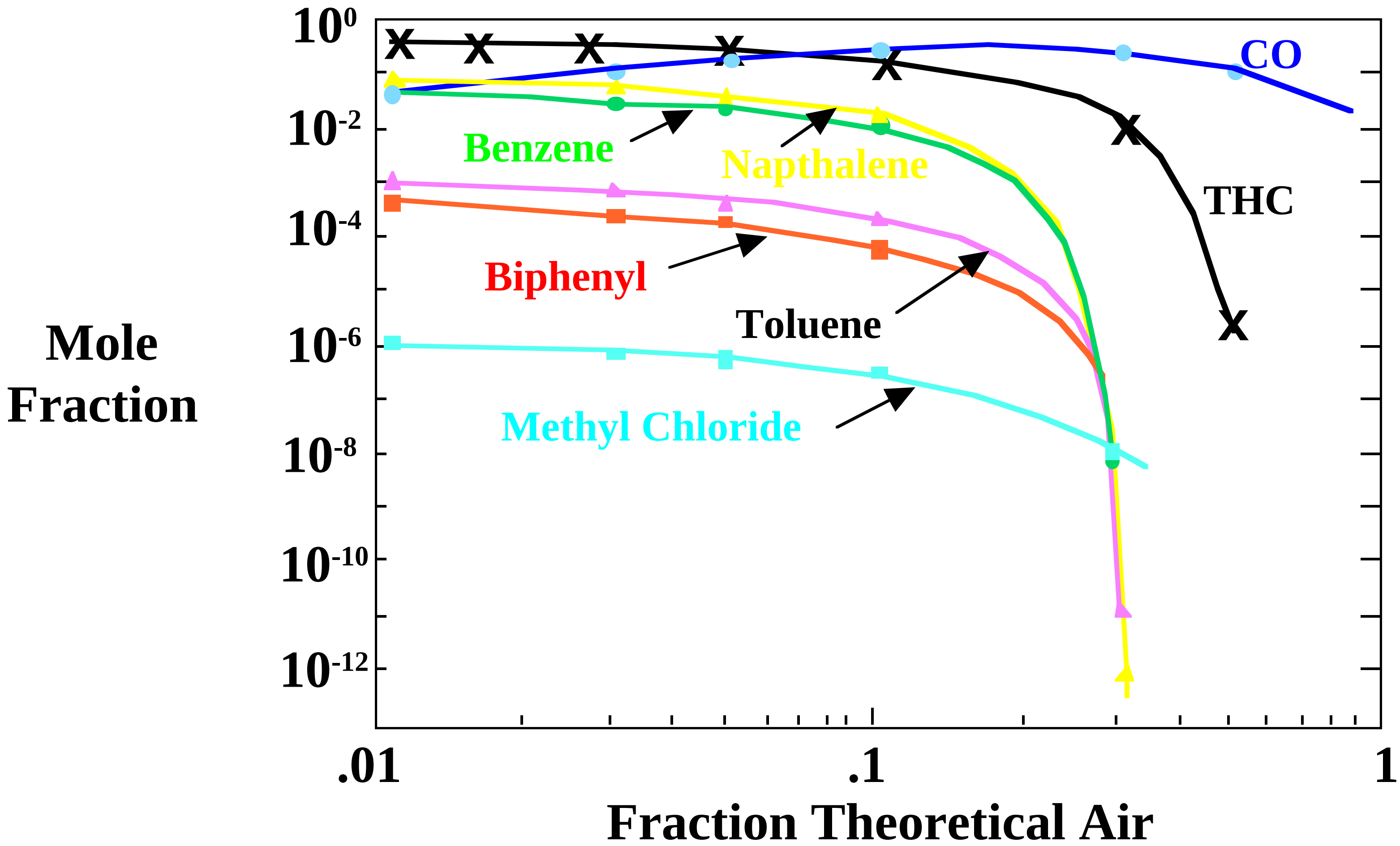
FUNDAMENTAL PRINCIPLES

❑ Organics

- *Under combustion conditions (high temperatures and with available oxygen),*
  - thermodynamic equilibrium levels of organics are negligible
  - flame/oxidation chemistry of destruction is fast
- *Formation results from poor mixing, quenches, cool temperature pathways, gas-particle interactions, lack of particle burnout, sooting.*

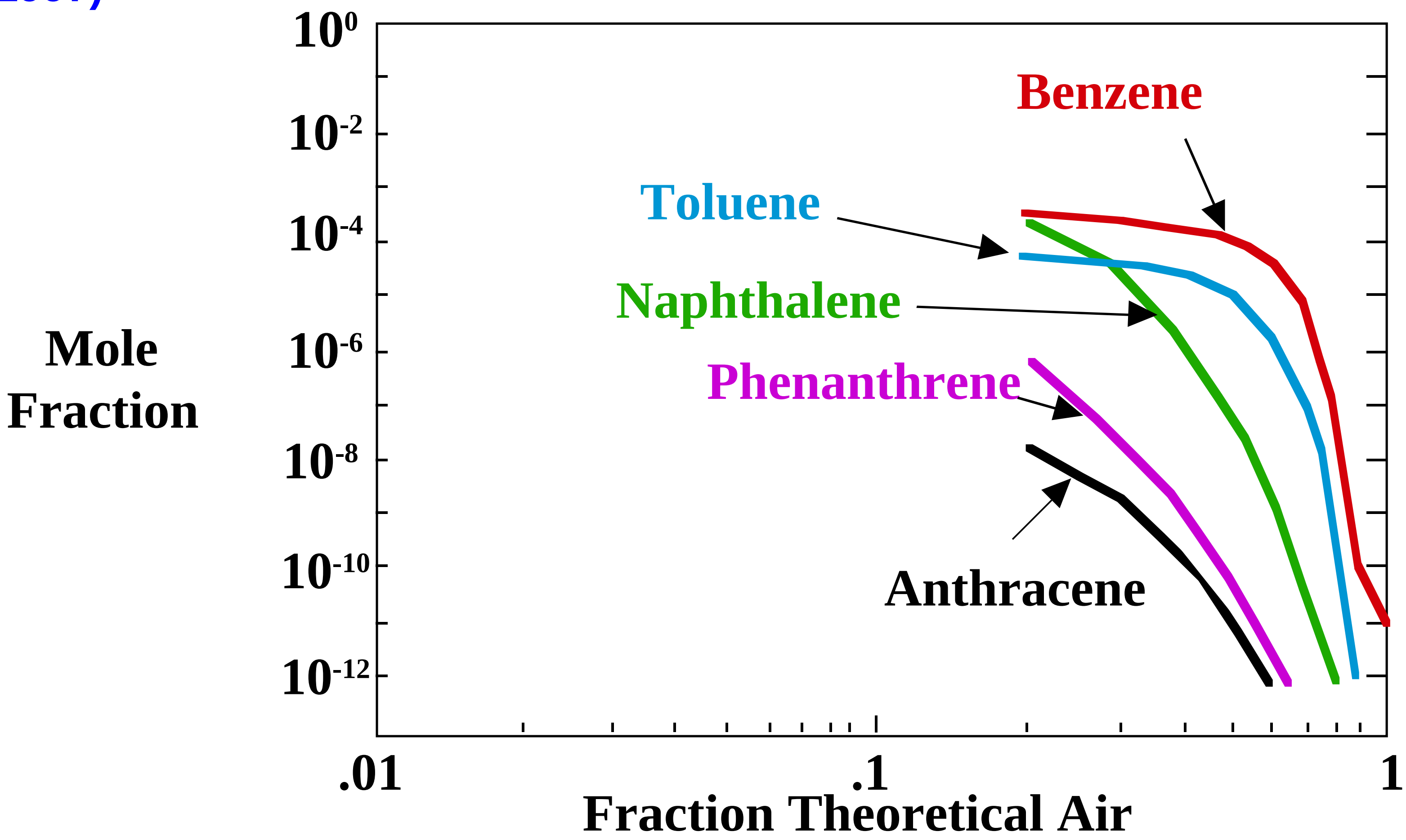
THERMODYNAMICS

- Equilibrium levels very low except for very rich conditions



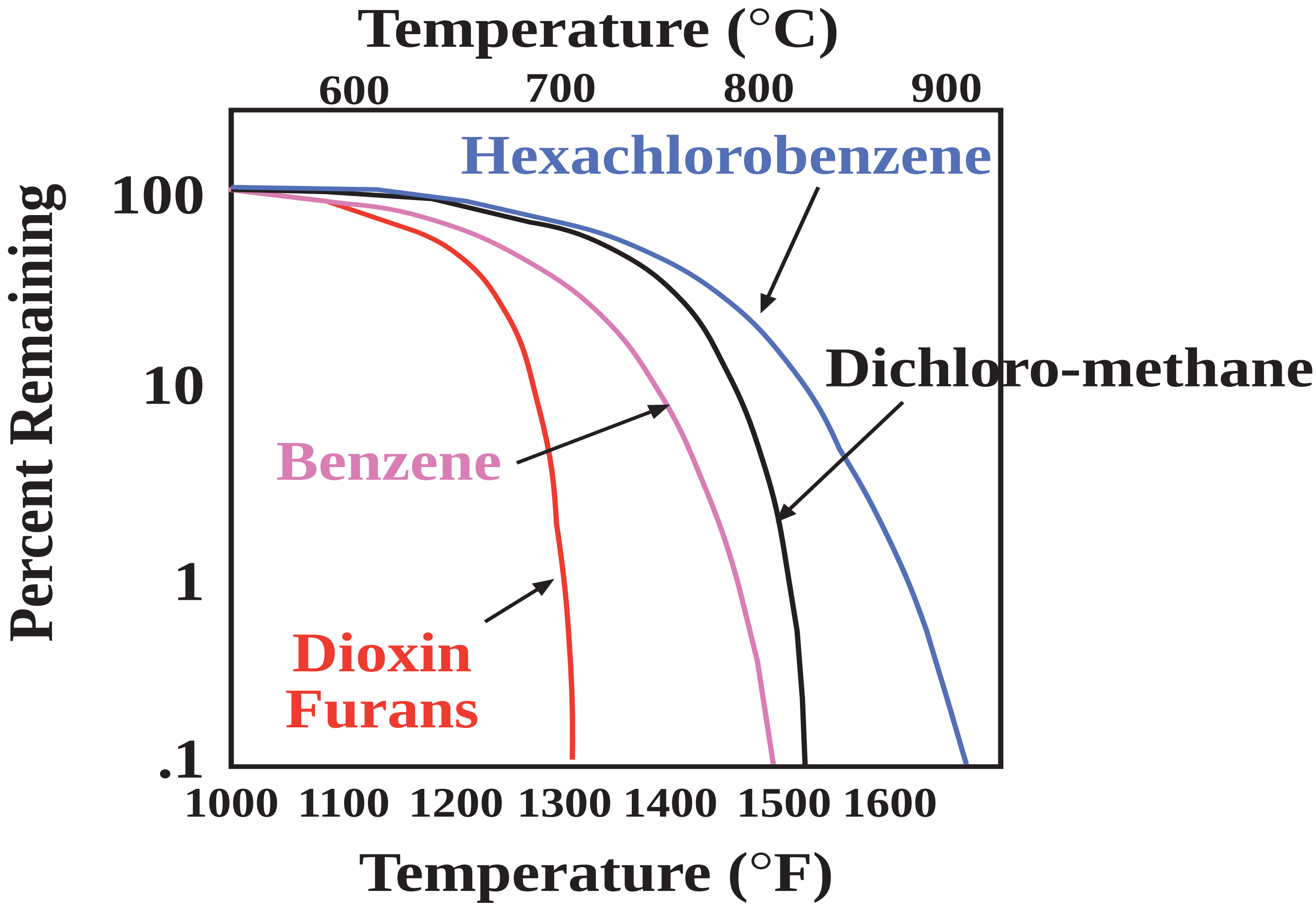
ORGANIC KINETICS

- Rapid Destruction Kinetics (modeling data 1227°C, 2240°F for 10 msec in stirred reactor, after W.J. Pitz et al, 1997)



DESTRUCTION KINETICS

- Rapid Destruction Kinetics (Flow Reactor Data, After Dellinger et al 1977)



SOURCES AND CONDITIONS FOR ORGANIC HAPS

- **From Unburned Fuel**
  - ***e.g., Benzene, Toluene, Ethylbenzene and Xylene (BTEX), hexane, naphthalene***
- **From Quenches**
  - ***e.g., acetaldehydes, formaldehydes, acrolein***
  - ***also CO***
- **From By-product Chemistry in Rich Packets**
  - ***e.g., benzene and toluene***
  - ***e.g., polyaromatic hydrocarbons***
- **From Gas-Particle Interactions**
  - ***e.g., chlorinated dioxin***

OUTLINE OF TALK

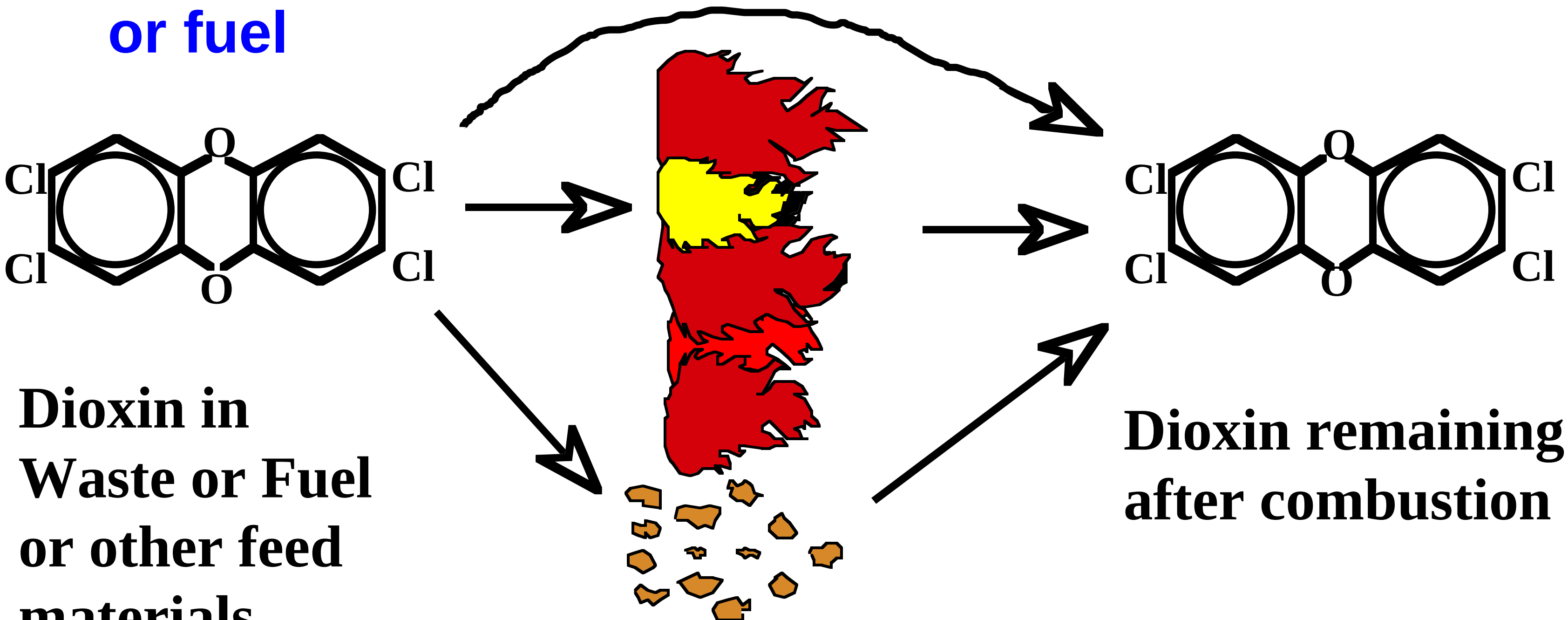
- Structures
- Concentrations of interest
- Measurement Techniques and Issues
- Fundamental Principles
- **Dioxin and Furan Formation Chemistry**
- Control Technologies
- Formation Conditions
- Monitoring Technologies
- Conclusions
- Recommendations

DIOXIN FORMATION MECHANISM

- **1. Undestroyed PCDD/PCDF originating with waste or fuel**
- **2. Gas Phase Formation (Furnace to 500°C)**
  - ***From Related Chlorinated Precursors and from Simple Organics and Chlorine Donors (ca. 700°C)***
  - ***Formation of Dioxin or Precursors from Complex Organics and Chlorine Donors***
- **3. Solid Phase Particle Mechanisms (< 500°C)**
  - ***de novo synthesis***
  - ***Catalyzed Precursor Mechanisms***
  - ***Condensation of Precursors and surface chlorination***

DIOXIN FORMATION MECHANISMS

- 1. Undestroyed PCDD/PCDF originating with waste or fuel



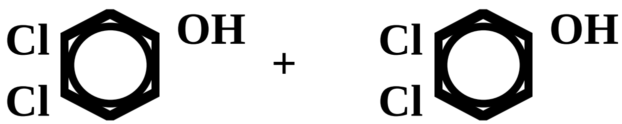
Failure Modes e.g.,

- flame bypass
- low temperature
- poor mixing
- particulate burnout
- quenches

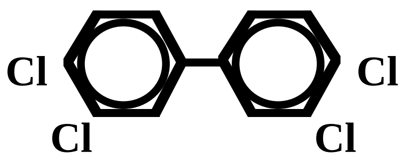
DIOXIN FORMATION MECHANISMS

❑ 2. Gas Phase Formation

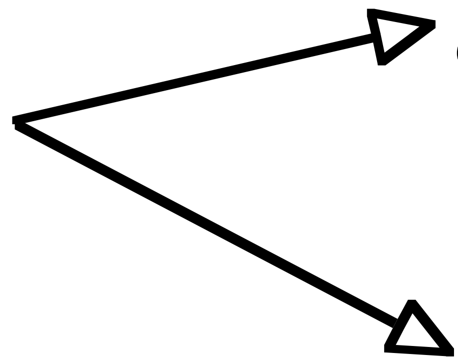
➪ ***from Related Chlorinated Precursors and from Organics and Chlorine Donors (ca. 700°C)***

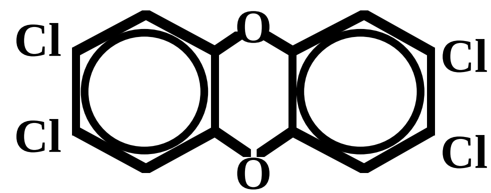


Chlorophenols



PCB





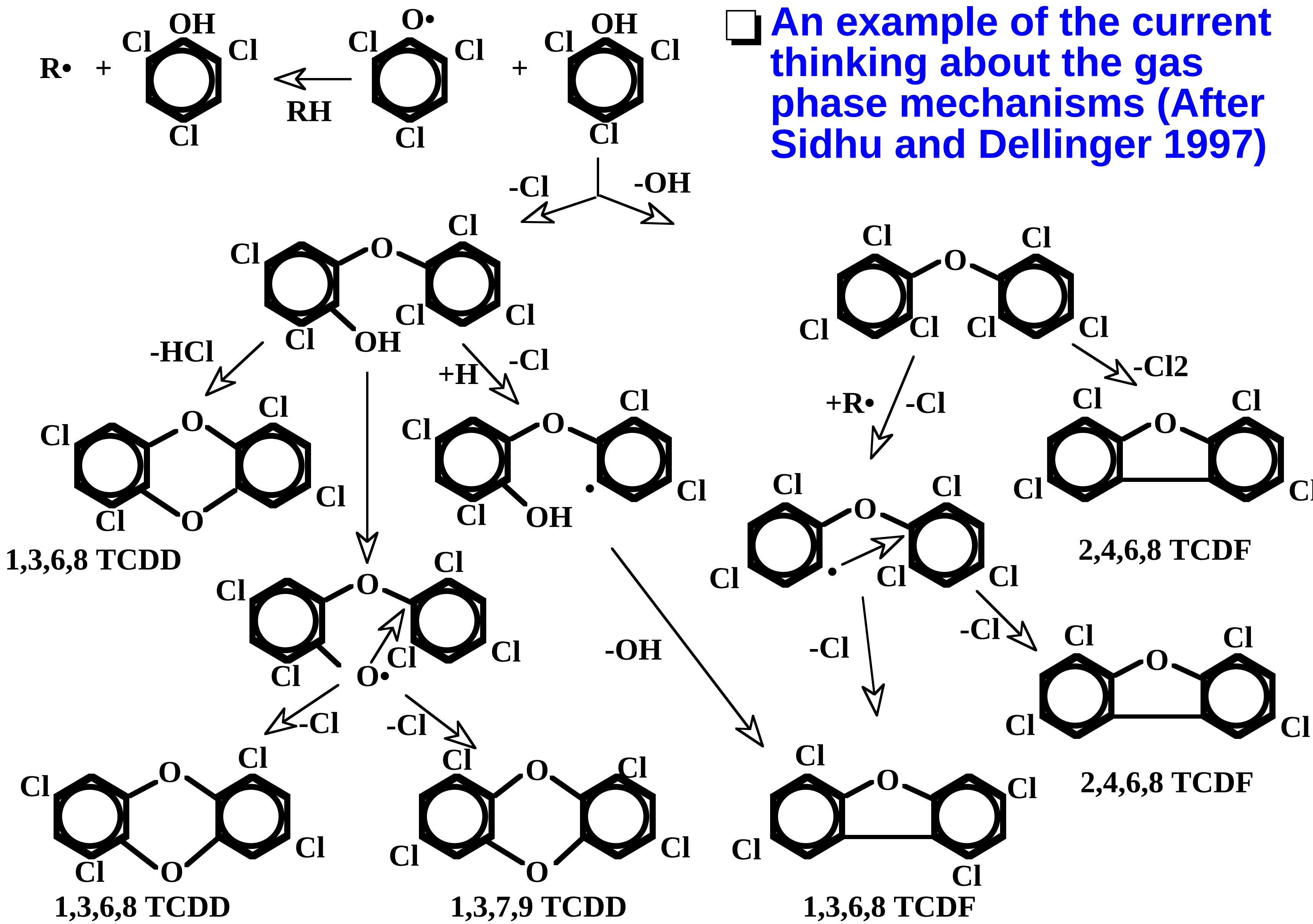
Precursors for downstream formation

Evidence: PCDD/PCDF on soot from PCB fires

Lab and Bench Scale Studies of PCB, Chlorinated Benzene, Chlorinated Phenols, C_2 aliphatics have yielded PCDD/PCDF (e.g., Schaub and Tsang, Sidhu and Dellinger, Grotheer and Louw, Akki and Mulholland, Weber)

GAS PHASE MECHANISMS

- An example of the current thinking about the gas phase mechanisms (After Sidhu and Dellinger 1997)



DIOXIN FORMATION MECHANISMS

2. Gas Phase Mechanisms

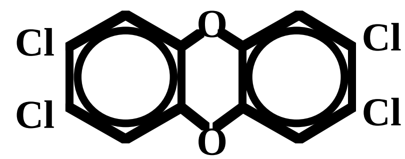
- *Formation of Dioxin or Precursors from Organics and Chlorine Donors*

Complex Organic Structure
Lignin
Wood
Paper
Plastics

+

Chlorine Donor
PVC
NaCl
HCl/Cl2

→



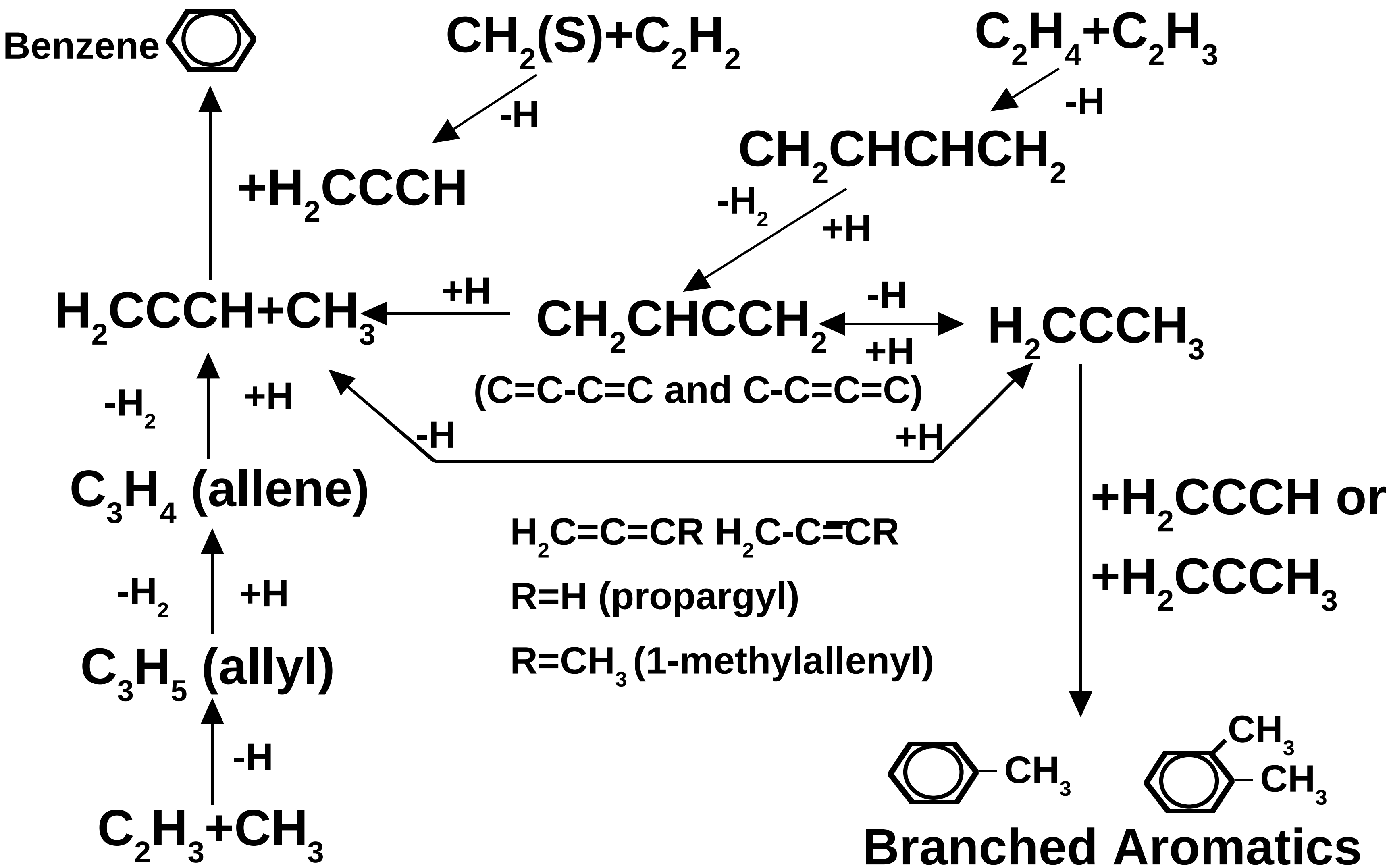
Precursors for downstream formation

Evidence: **Lab scale tests of vegetable matter, wood, lignin, coal with chlorine source have yielded PCDD/PCDF**

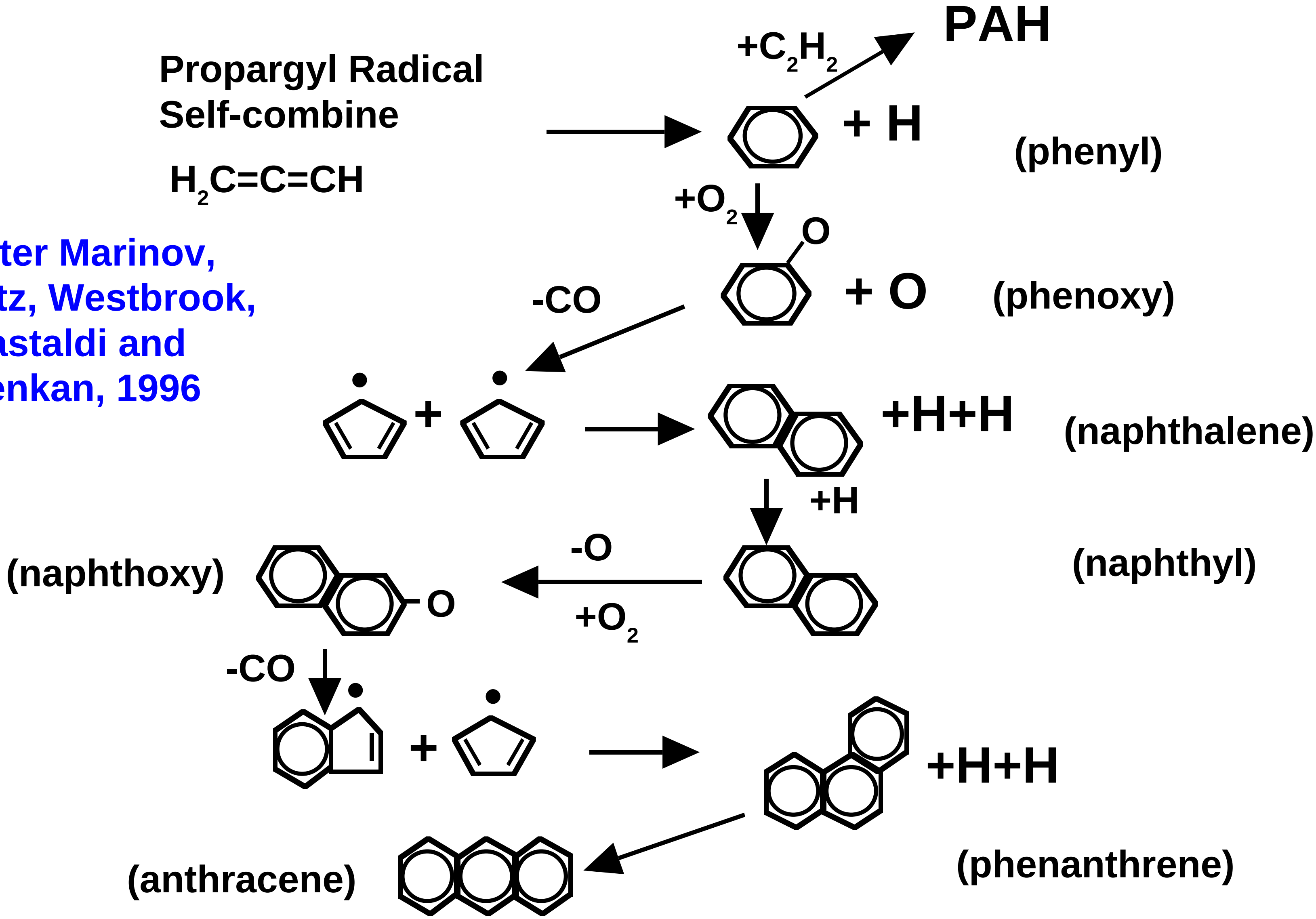
Lab scale studies on fuel rich, simple hydrocarbon flames yielded PAH (e.g., Marinov, et al and Senkan et al)

FUEL RICH FORMATION PATHWAYS FOR AROMATICS

After Marinov, Pitz, Westbrook, Castaldi and Senkan, 1996



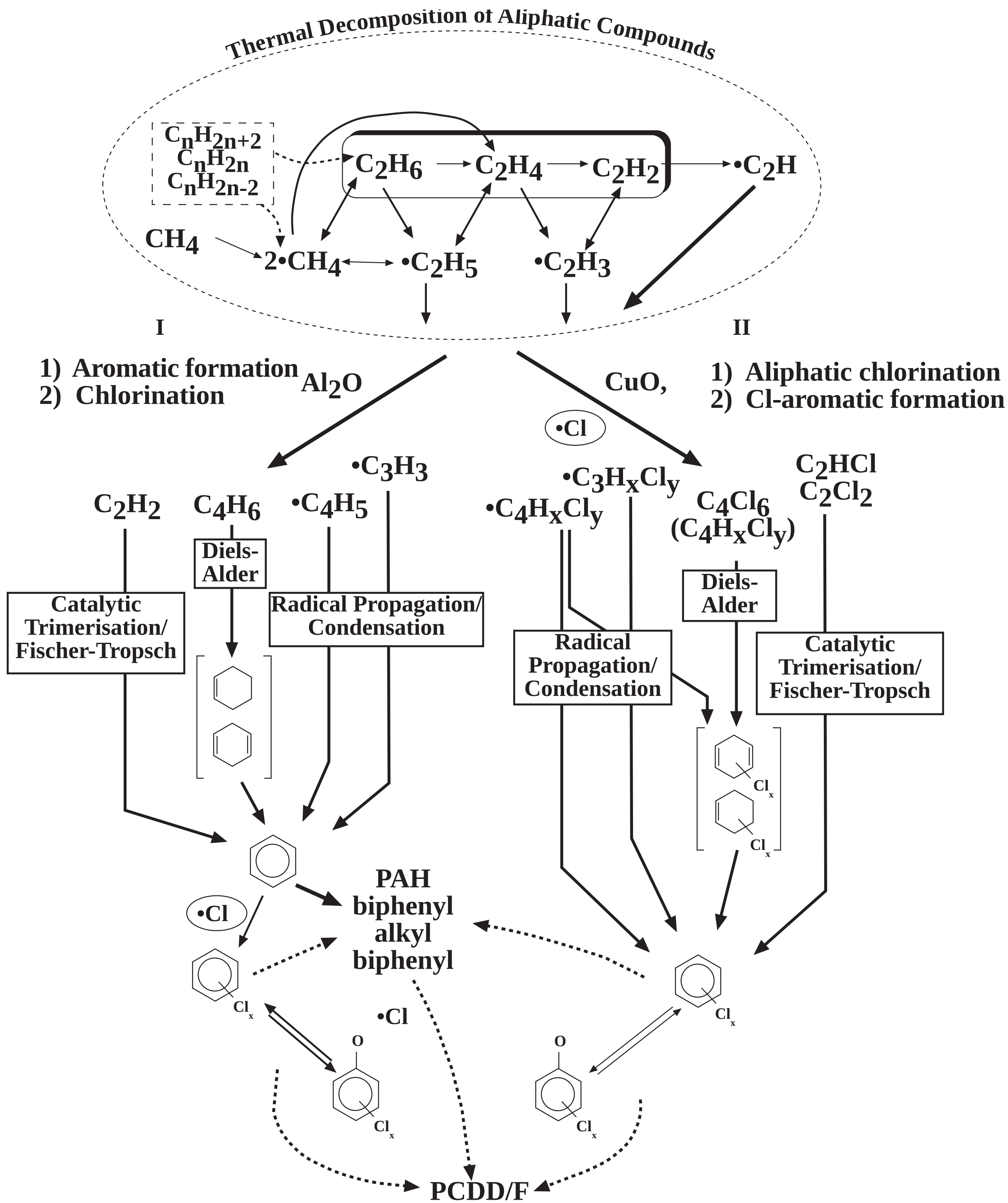
FUEL RICH PAH FORMATION PATHWAYS



After Marinov, Pitz, Westbrook, Castaldi and Senkan, 1996

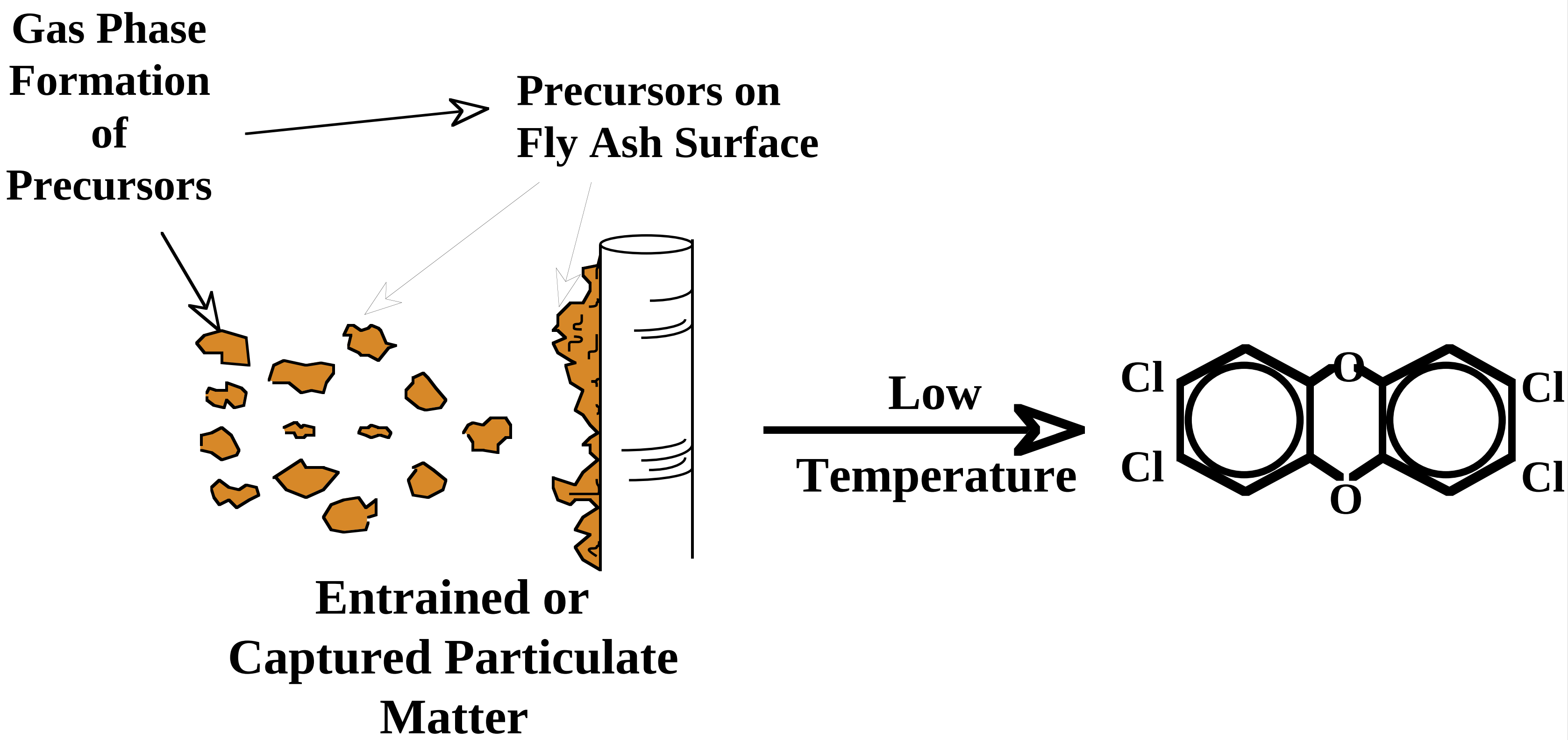
GAS PHASE MECHANISMS

Heterogeneous combustion reactions of C2 aliphatics (ca 600°C) (After Froese and Hutzinger, 1997)



DIOXIN FORMATION MECHANISMS

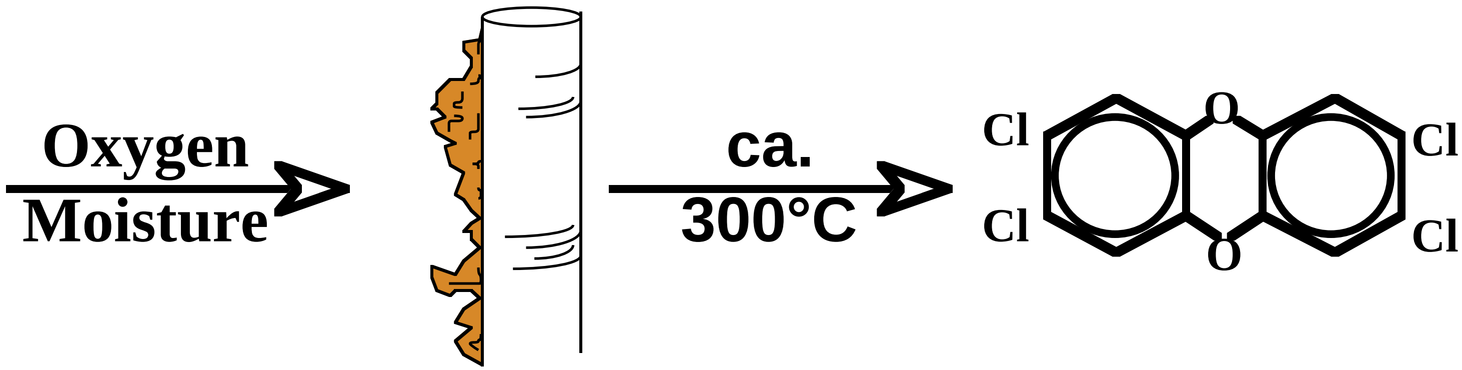
❑ 3. Solid Phase Particle Mechanisms (< 500 °C)



DIOXIN FORMATION MECHANISMS

3a. de novo synthesis

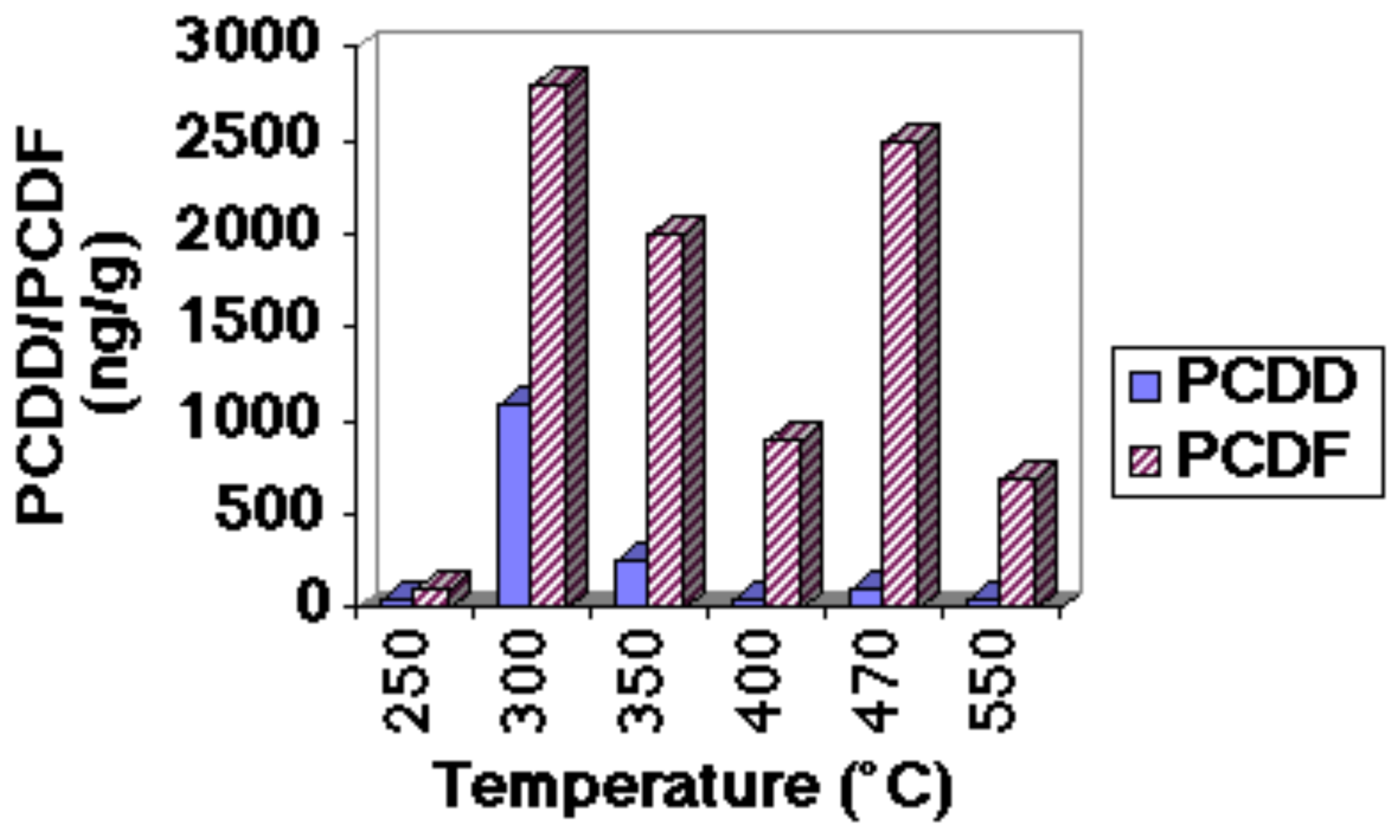
- *fly ash can be source of carbon, catalysts and chlorine as reagent for low temperature formation (ca. 300 °C)*
- *oxidative gasification reactions with carbon in particles to cleave dioxin/furan structures*



Evidence: Laboratory scale tests of heated fly ash can generate PCDDPCDF

DE NOVO FORMATION

- Effect of Temperature on de novo formation rates of tetra- to octa- PCDD/PCDF (Schwartz 1990)



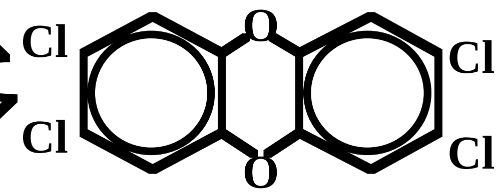
DIOXIN FORMATION MECHANISMS

❑ 3b. Catalyzed Precursor Mechanisms (< 500 °C)

Chlorinated Precursors (e.g., Chlorophenols)

NonChlorinated Precursors (e.g., Aliphatics, Aromatices, Propene, Benzene C_2 hydrocarbons, Methane) + **Chlorine Source**

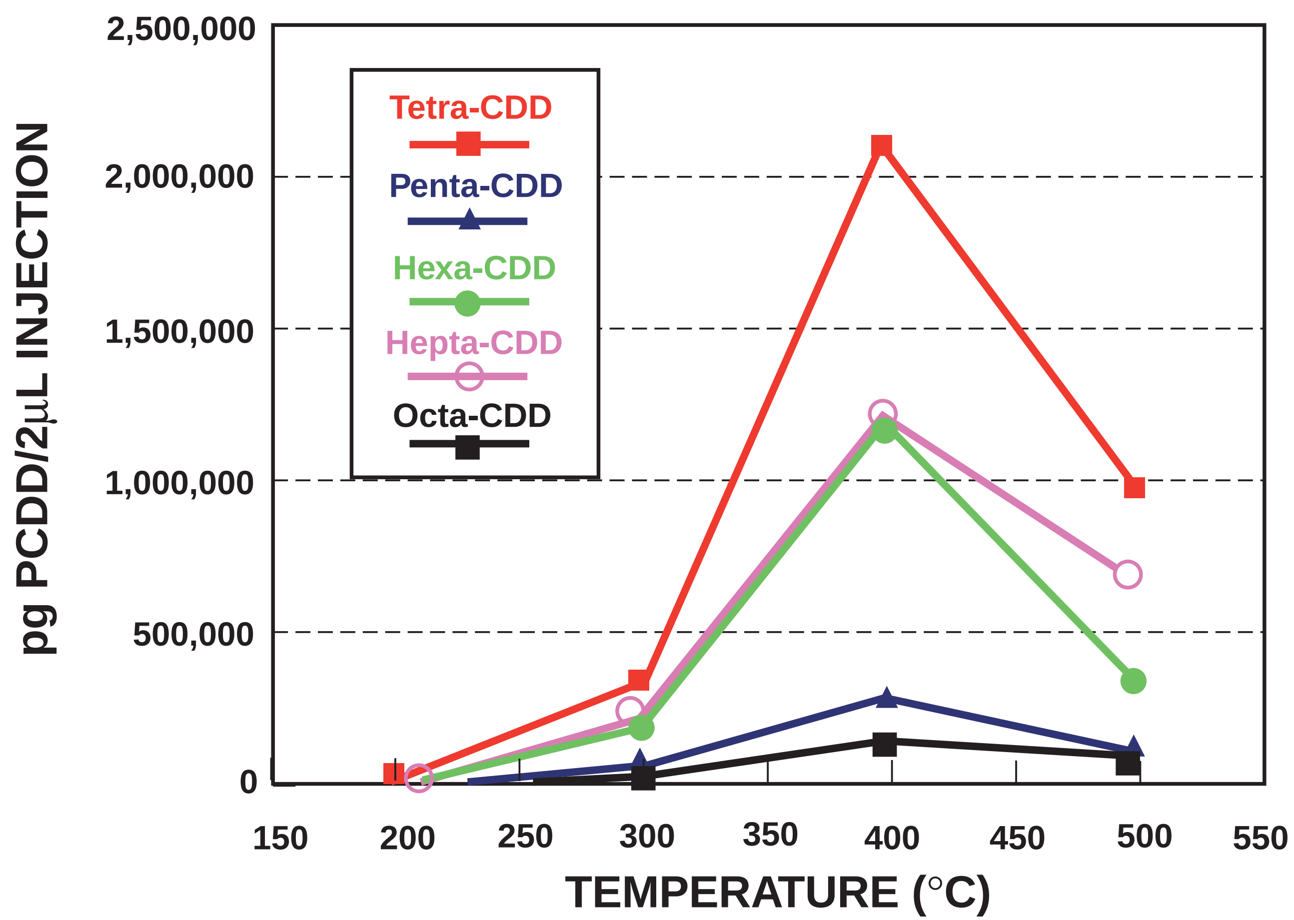
Metal Catalyzed



Evidence: Lab Scale data where PCDD/PCDF has been generated at low temperatures when different organics have been burned in the presence of chlorine sources and metals (e.g., Gullett, Froese, Addink)

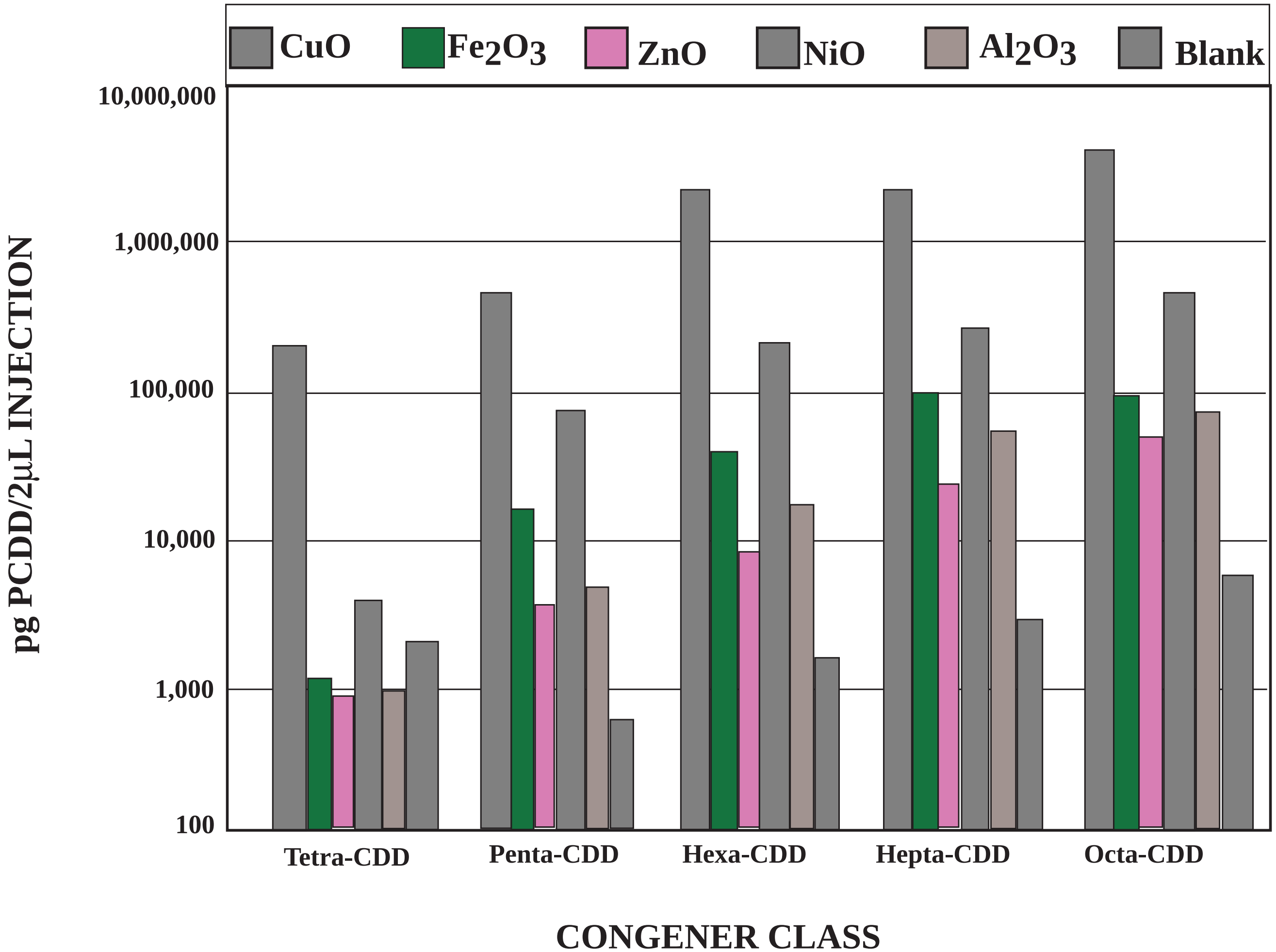
CATALYZED PRECURSOR MECHANISMS

- Effect of Temperature on production with Cu(II) with chlorophenol



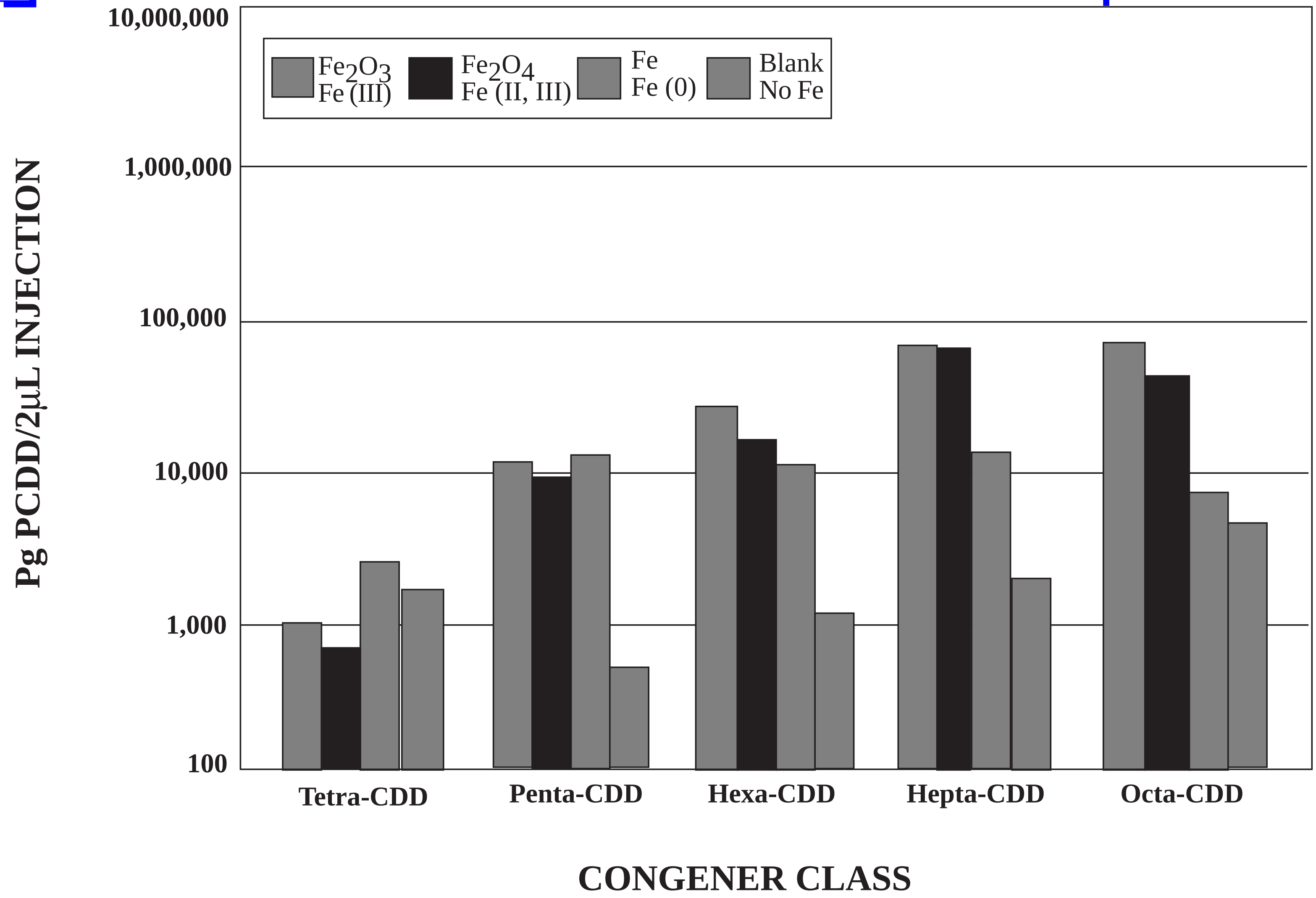
CATALYZED PRECURSOR MECHANISMS

- Effect of various metals on dioxin formation from chlorinated phenol



CATALYZED PRECURSOR MECHANISMS

❑ Effect of iron oxidative state on PCDD with chlorophenol



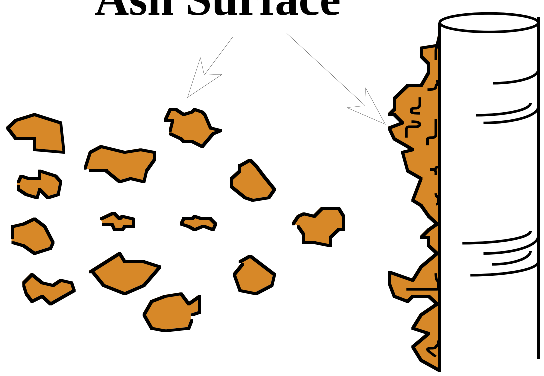
ICCR Meeting September 17,1997

DIOXIN FORMATION MECHANISMS

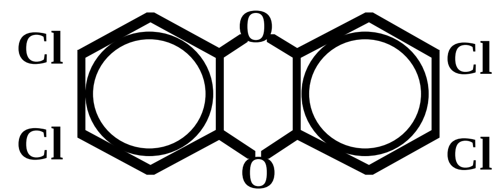
3c. Condensation of Precursors and Surface Chlorination (< 500°C)

- *Surface condensation of precursors followed by direct chlorination of adsorbed hydrocarbons*

Precursors condense on Fly Ash Surface



+ **Surface Chlorine Donor** —Low Temperature→

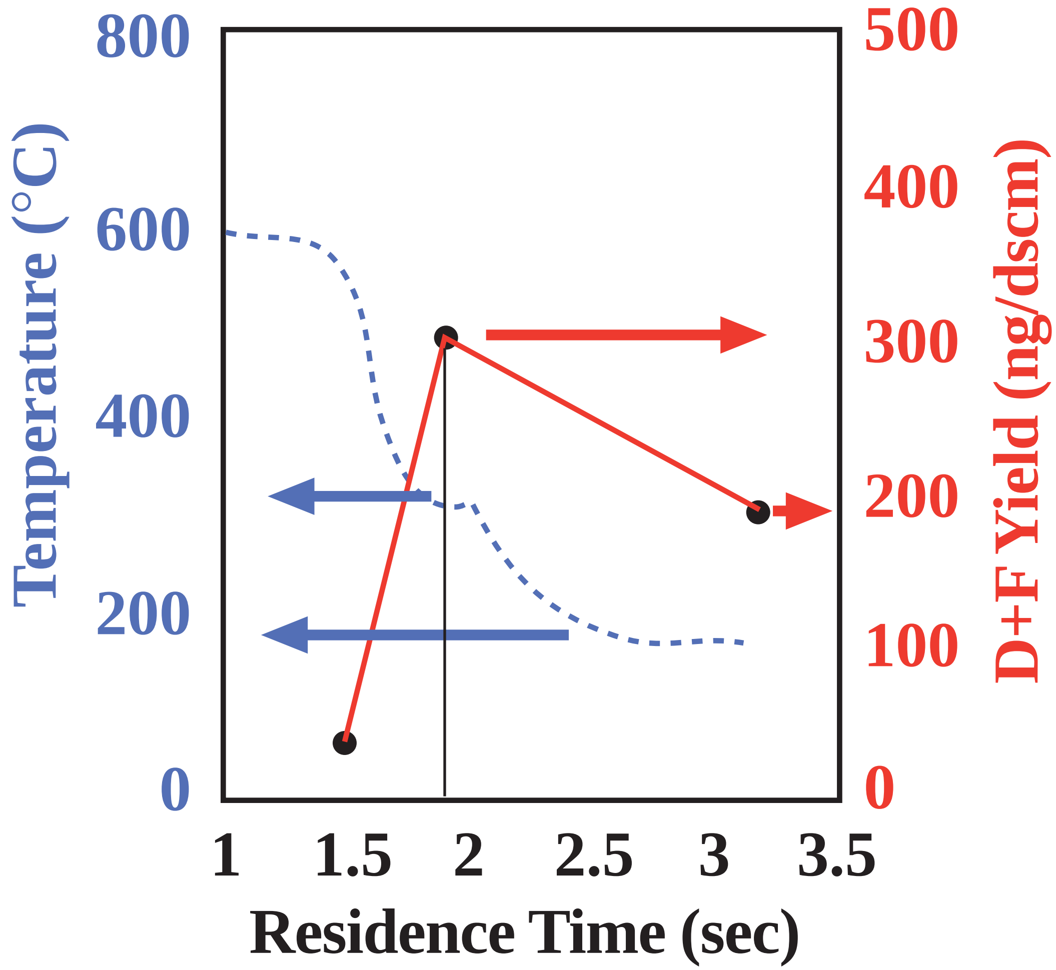


Entrained or Captured Particulate Matter

Evidence: Studies of passing combustion effluents with oxygen and HCl over fly ash (Altwicker) and entrained flow studies (Gullett et al)

IN FLIGHT FORMATION

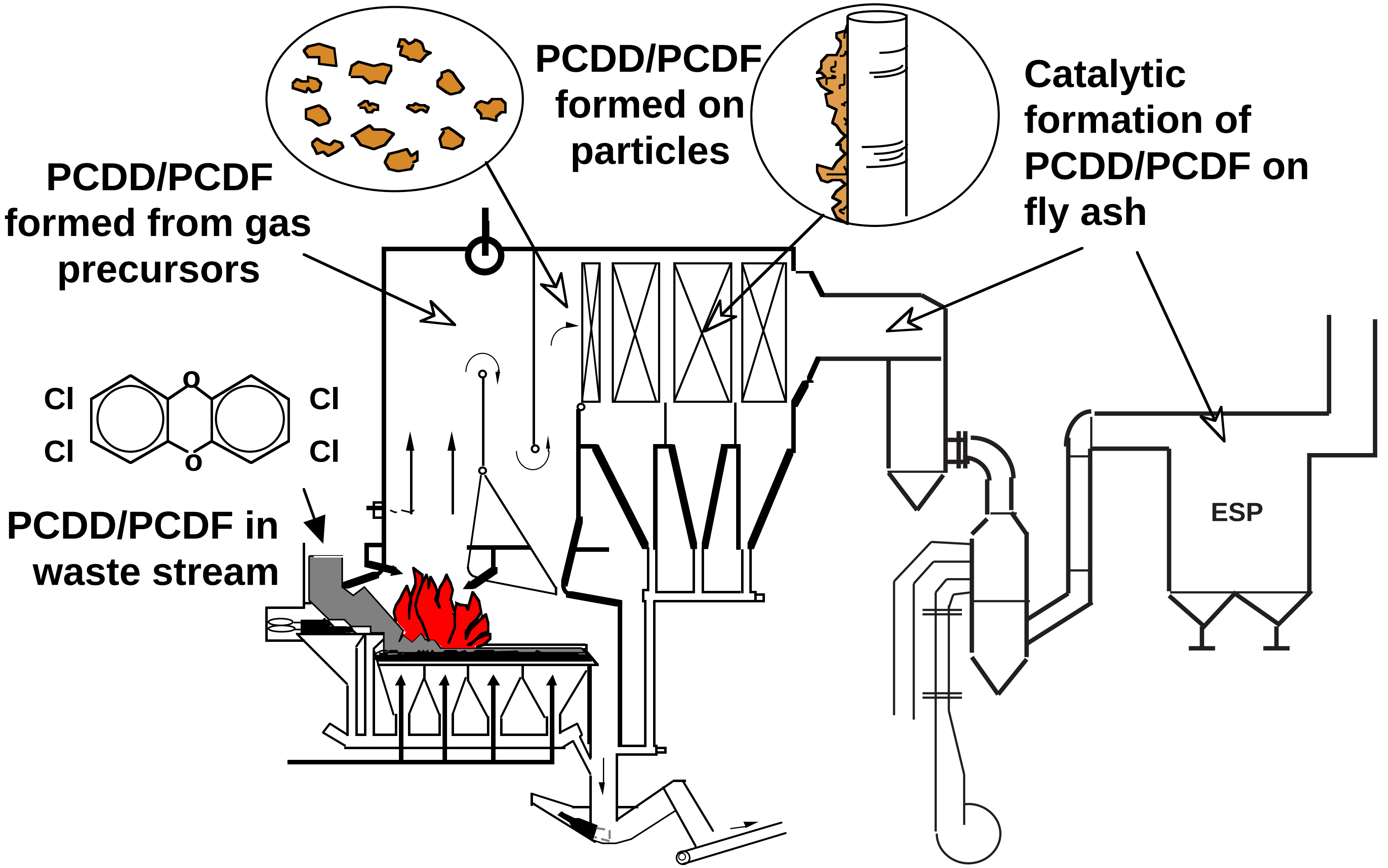
- ❑ Pilot Scale RDF Combustion Tests (After Gullett, 1997)
- ❑ PCDD/PCDF has formed by 325 °C
- ❑ Levels decline with time
- ❑ Long residence times in APCD are not necessarily required for formation



OUTLINE OF TALK

- Structures
- Concentrations of interest
- Measurement Techniques and Issues
- Fundamental Principles
- Dioxin and Furan Formation Chemistry
- Control Technologies
- Formation Conditions
- Monitoring Technologies
- Conclusions
- Recommendations

DIOXIN FORMATION MECHANISM REGIONS



SIGNIFICANT PARAMETERS - FIELD STUDIES

Parameter	Observation	Source
Entrained PM	Increase Stack PCDD/F Furnace formed PCDD/F associated with Particles	Quebec City,MWC Montgomery Cty, MWC
CO Emissions	Increase uncontrolled PCDD/F Low CO (<200 ppm) not sufficient to assure low stack PCDD/F High CO (>200 ppm) not sufficient to assure high PCDD/F	Mid-Conn, MWC Mid-Conn & Mont. Cty MWCs Various MWIs Cement kilns Utility boilers
Carbon in Fly Ash	Increase total PCDD/F formation Absorbs PCDD/F Diverts PCDD/F from stack to fly ash	Borgess Med Ctr Quebec City Davis County

SIGNIFICANT PARAMETERS - FIELD STUDIES

Parameter	Observation	Source
APCD Temp.	PCDD/F Formation Increases Exponentially Effects solid/vapor phase partitioning	Montg. Cty, MWC Borgess, MWI Ash Grove , Ck Montg. Cty, MWC
Quench Rate	Rapid Quench decreases PCDD/F formation rate	MWIs & HWIs with wet scrubbers compared to units with heat recovery & dry APCD
Cl in Fuel	Negligible observed impact on PCDD/F stack emissions	Ash Grove Cement PPG HAF Wurtzberg, MWC HWIs with wet APCD
Catalytic Metals in fuel	Stack PCDD/F emissions impact not clearly defined	Quebec City, MWC Ash Grove Cement

PILOT SCALE PARAMETER SIGNIFICANCE

- Ability of specific parameters to account for observed PCDD/PCDF yields while holding all other parameters constant (semi-partial correlations from two separate pilot scale programs)

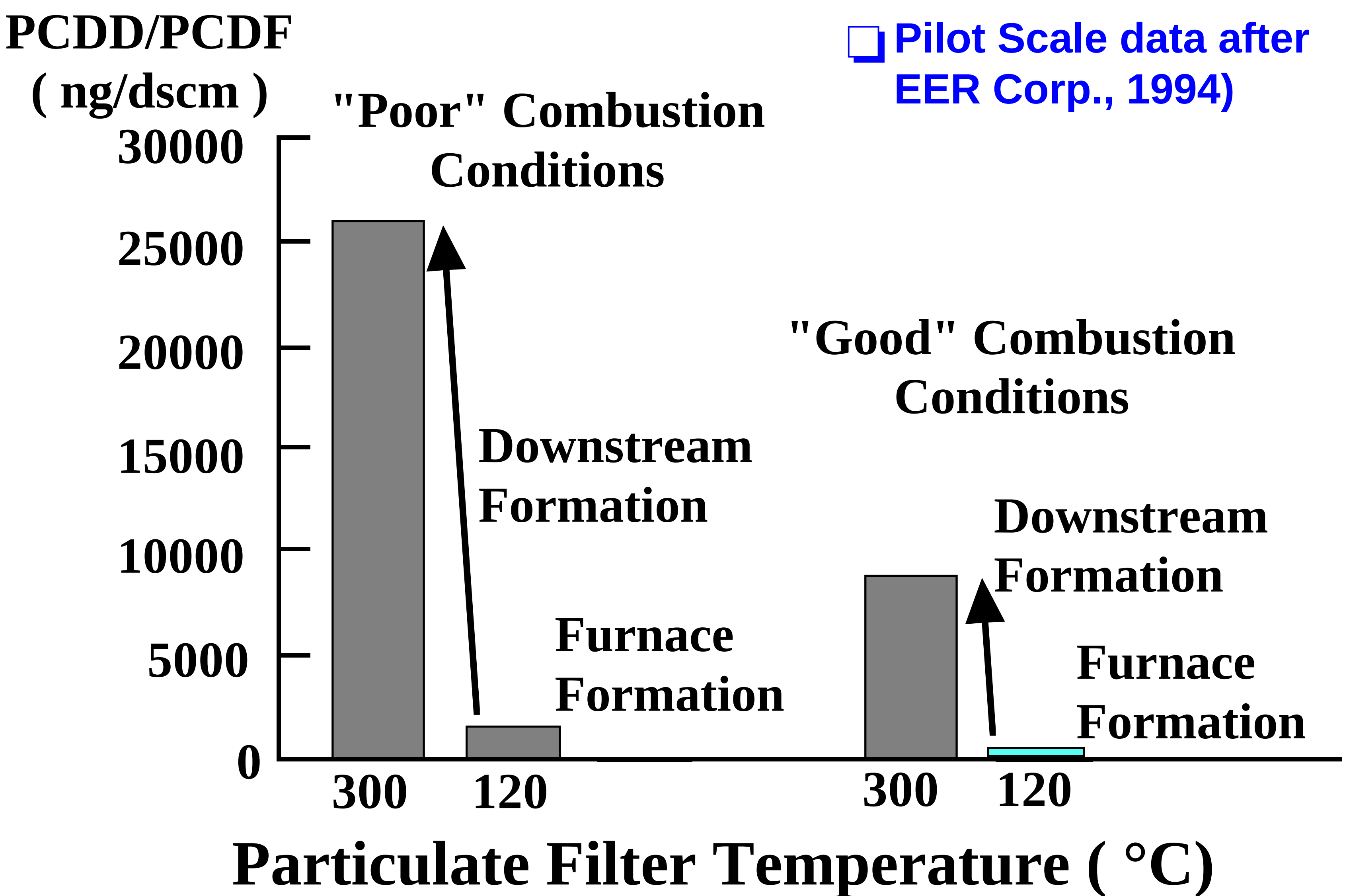
Parameter	RDF/Coal Co-Combustion	FlyAsh/Cl Injected into Natural Gas
RDF Feedrate	0.764	Not Considered
Quench Rate	0.762	0.271
Sorbent Injection	0.299	0.497
SO_2 Conc.	0.234	Not Considered
HCl Conc.	0.132	0.380
Sampling Temp.	0.016	Not Statistically Significant
Oxygen Conc.	Not Considered	0.092
Cl_2 Conc.	Not Considered	0.131
Duct Temp.	Not Considered	0.614
Residence Time	Not Statistically sig.	0.271

IMPORTANT CONTROLLING PARAMETERS

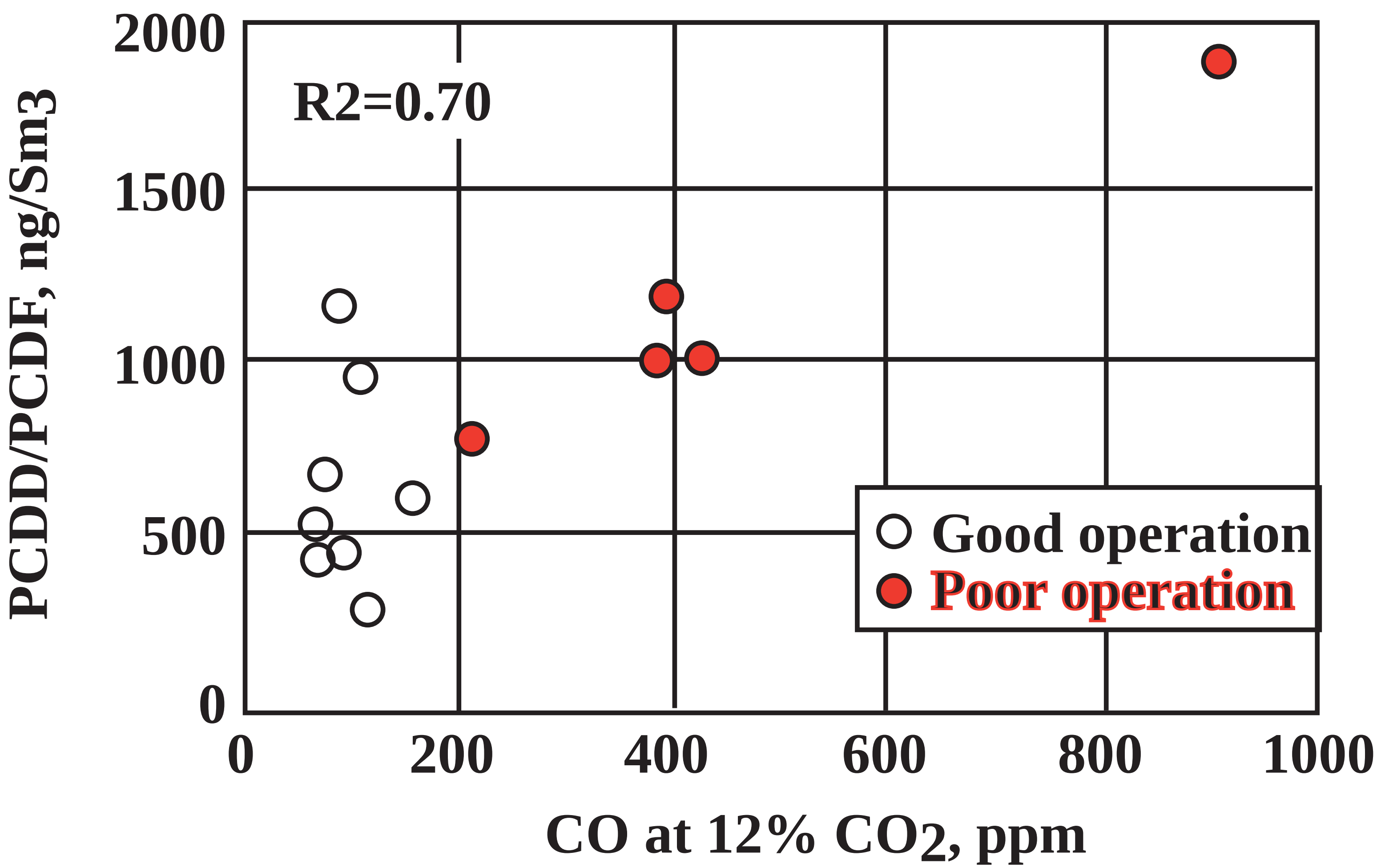
- Combustion conditions as indicated by
  - *CO and Total Hydrocarbon*
  - *Soot formation*
  - *Particle entrainment and burnout*
- Quench Rate and Air Pollution Control Temperature
- Fuel/waste parameters
  - *Chlorine*
  - *Sulfur*
  - *Metals*

ROLE OF COMBUSTION PRACTICE

❑ Pilot Scale data after EER Corp., 1994)

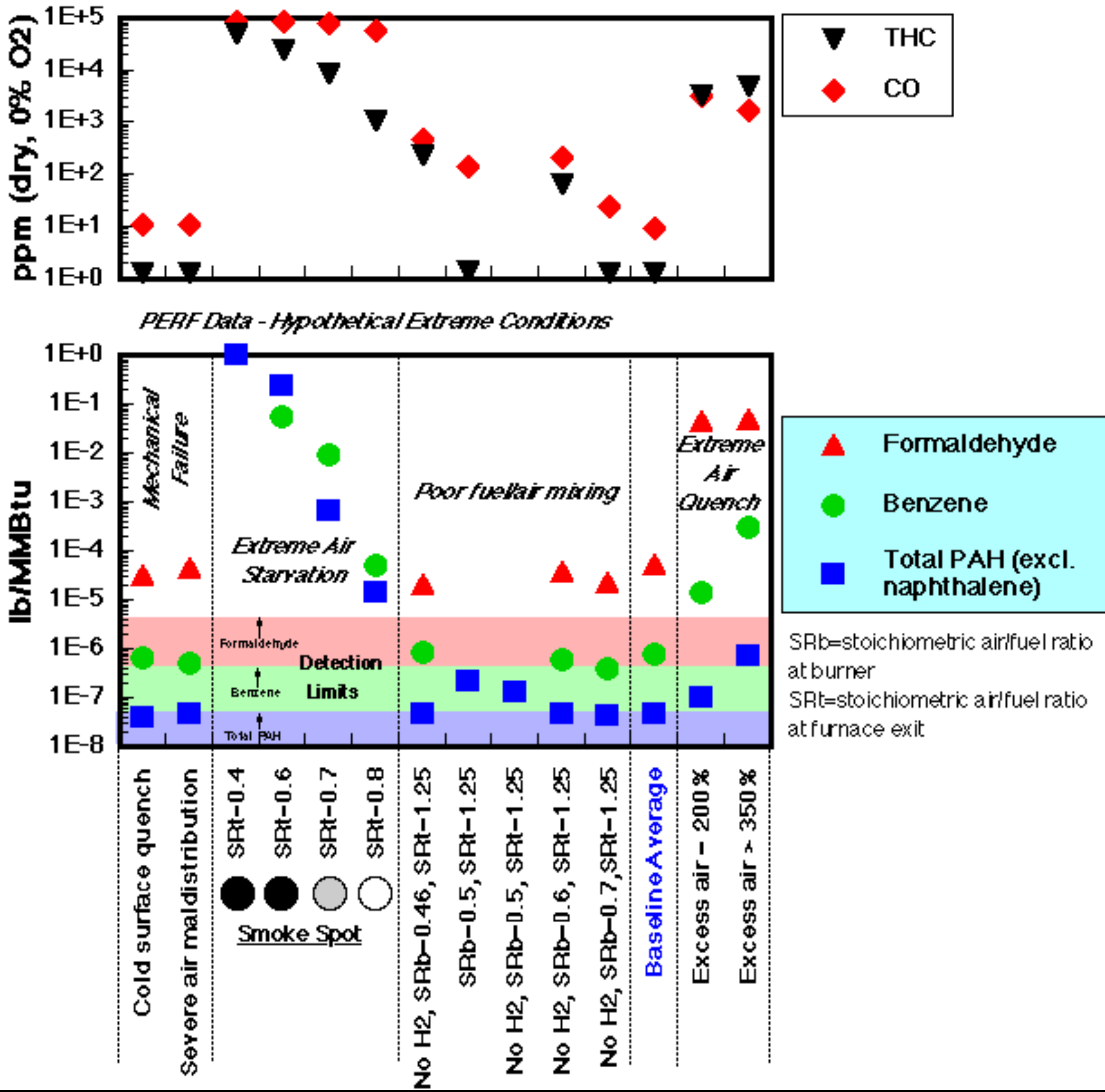


ROLE OF COMBUSTION PRACTICE



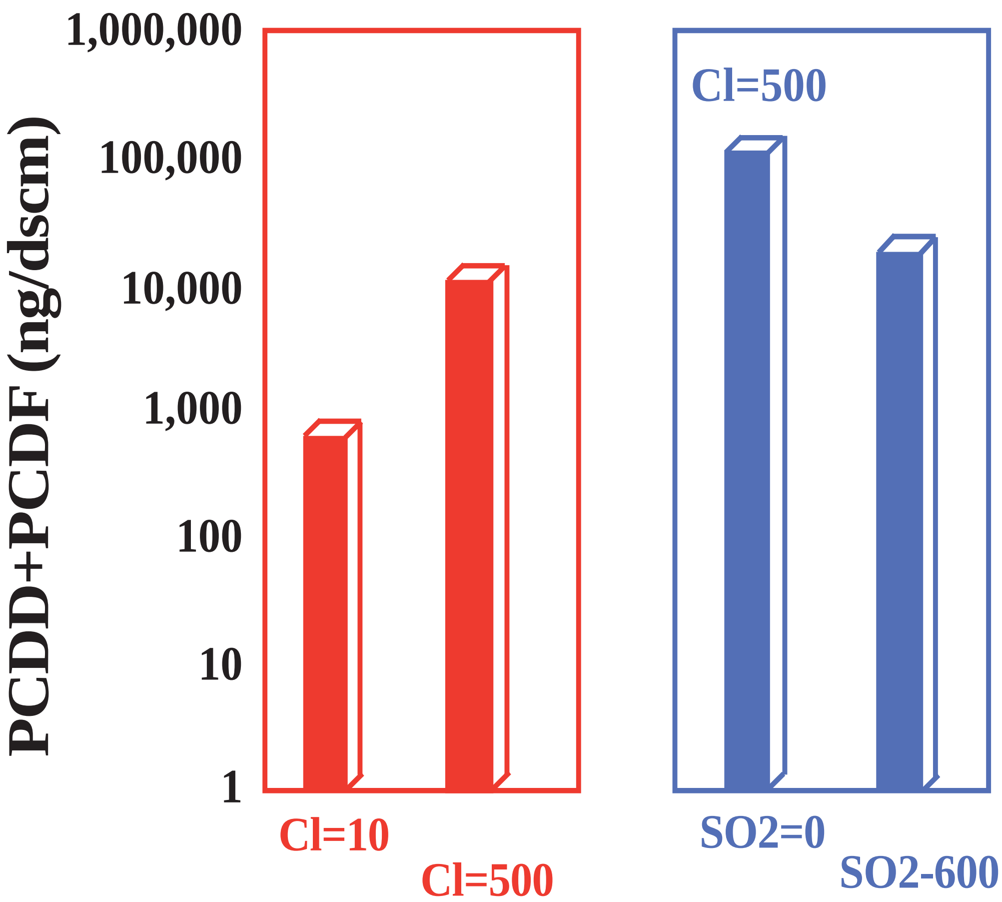
COMBUSTION CONDITIONS

- Laboratory Data- CO, THC and HAP
- Good Combustion Conditions as indicated by low CO and Total hydrocarbons leads to low HAP emissions
- After PERF, 1997



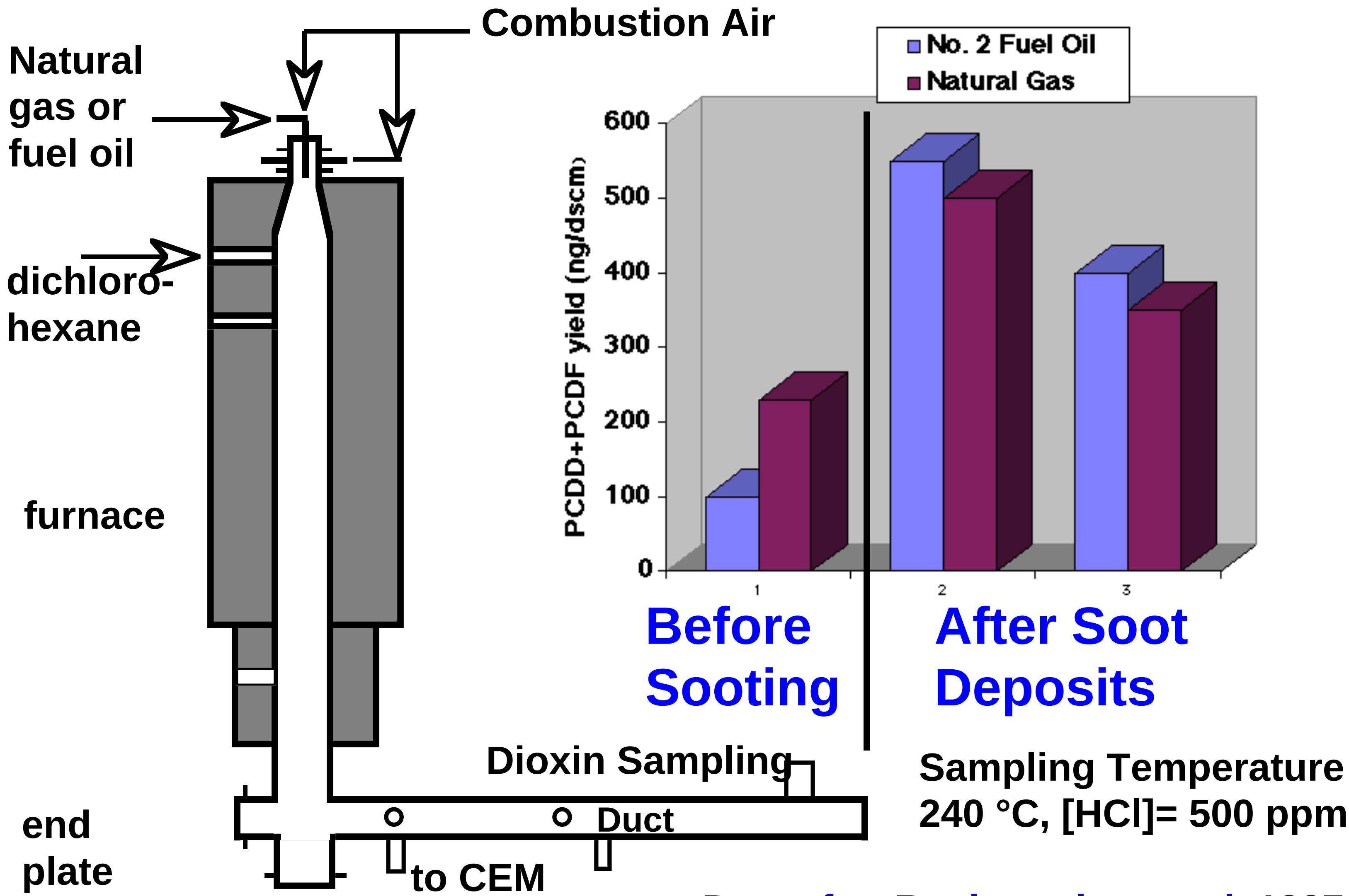
EFFECT OF SOOT DEPOSITS

- Boiler tube simulation with #2 fuel oil, copper napthenate, dichlorohexane
- Significant PCDD/PCDF formation
- Required all 3
  - *Soot*
  - *Copper*
  - *Chlorine*
- Formation even at low Cl (10ppm)
- Sulfur Dioxide suppresses PCDD/PCDF



Data after Raghunathan, Lee & Kilgroe, 1997

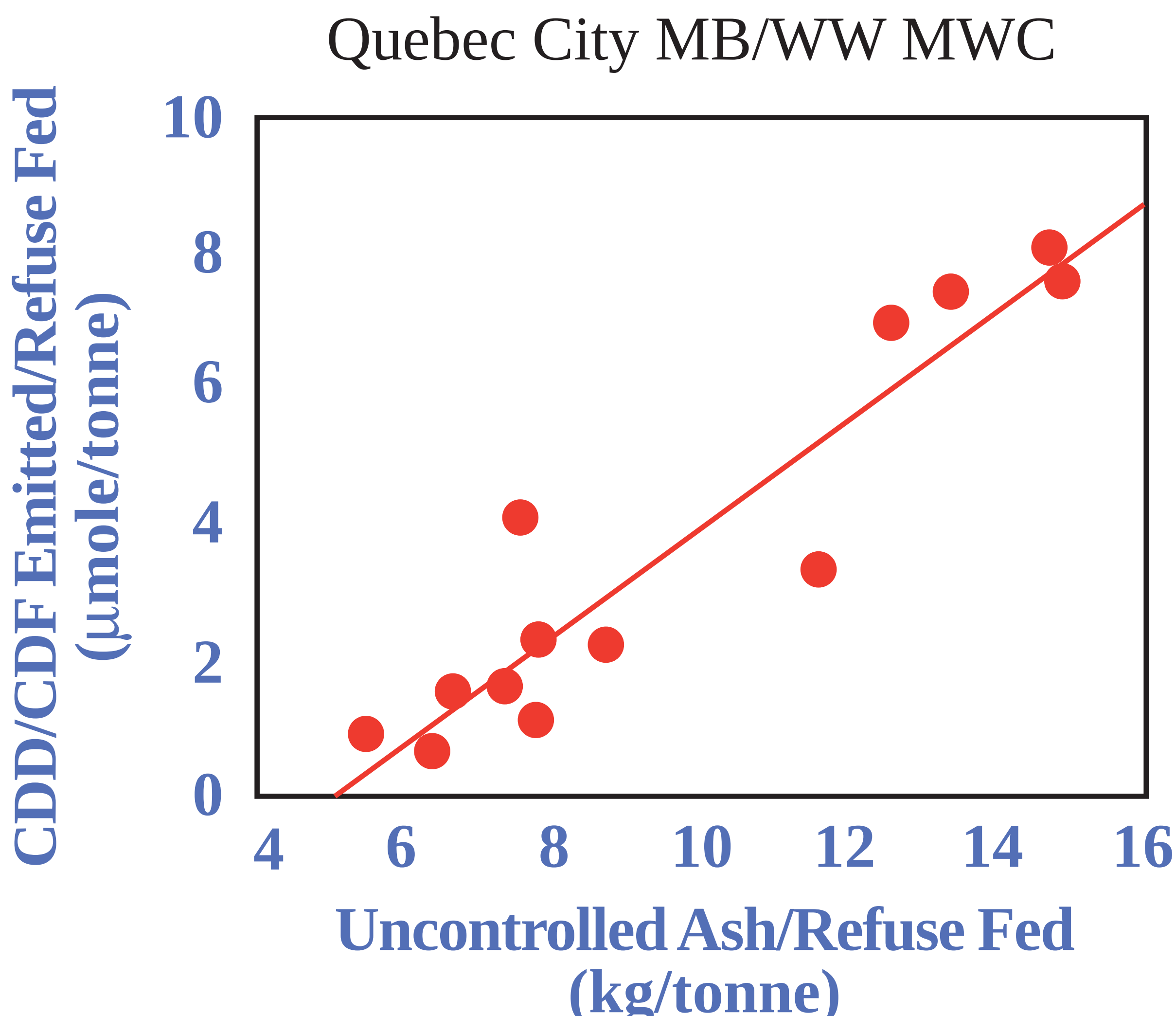
IMPACTS OF SOOT FORMATION



Sampling Temperature 240 °C, [HCl]= 500 ppm

Data after Raghunathan et al, 1997

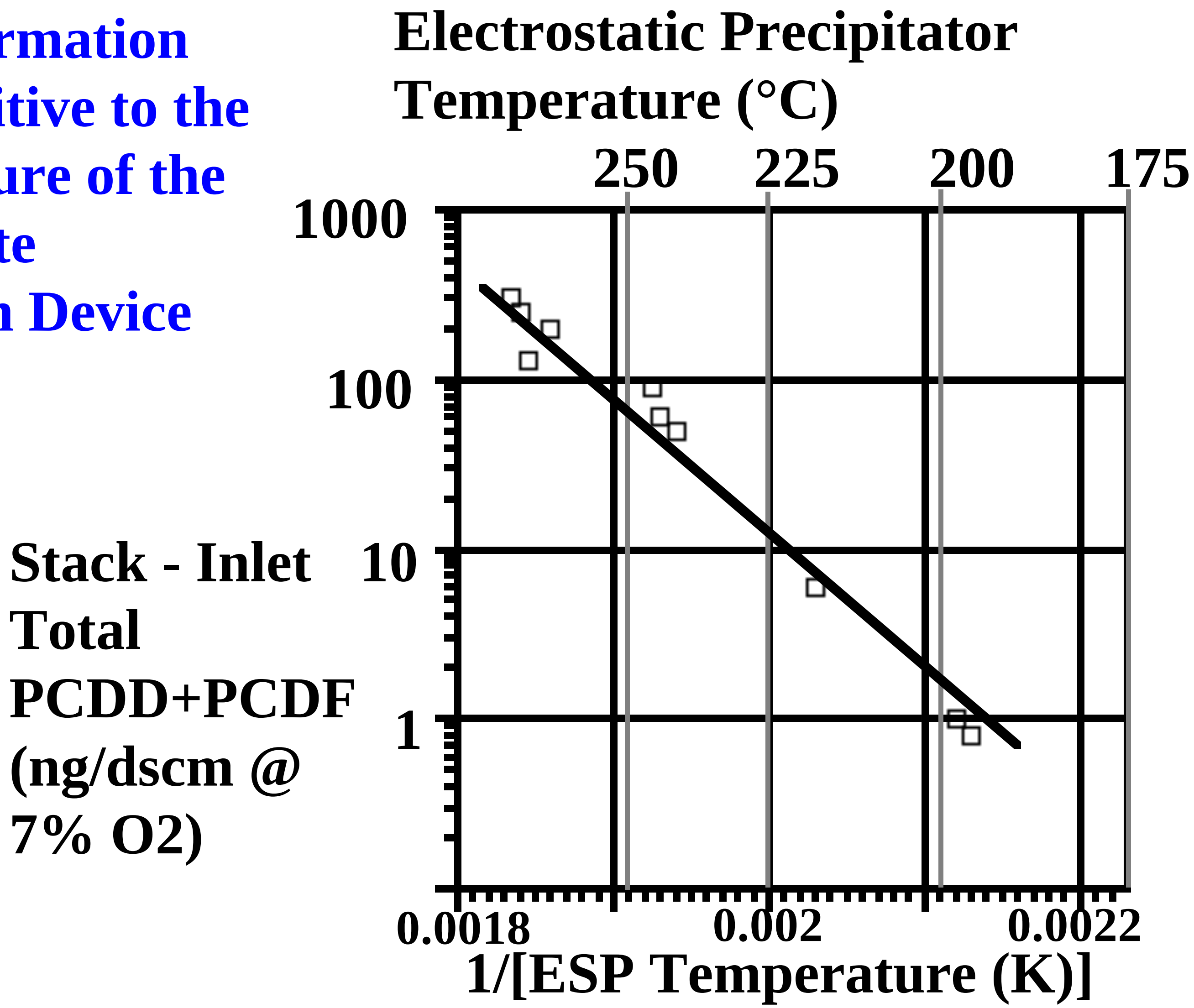
ROLE OF PARTICLES



Data after Barton et al, 1990

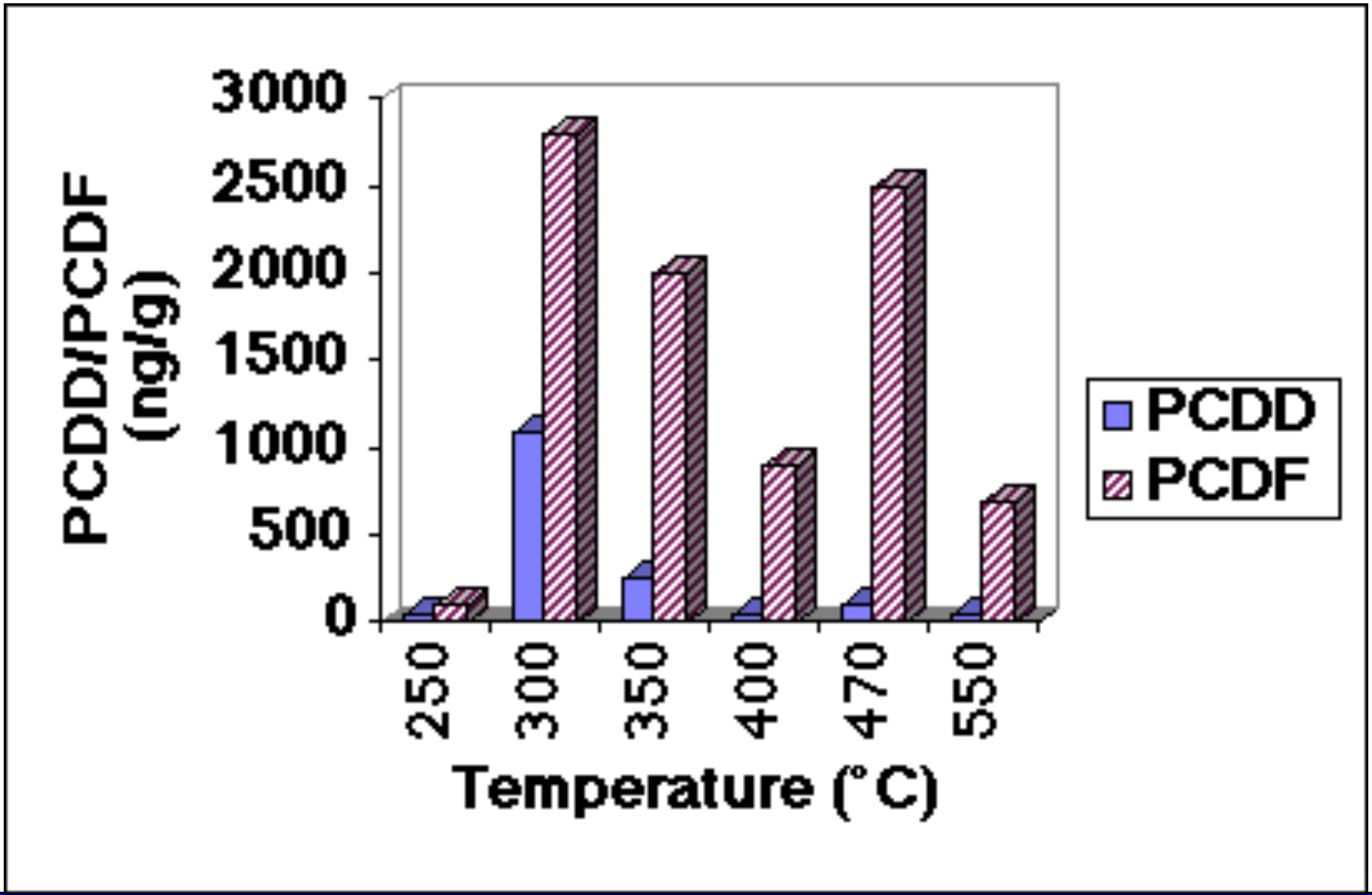
ROLE OF PARTICULATE CAPTURE TEMPERATURE

- Dioxin formation very sensitive to the temperature of the Particulate Collection Device

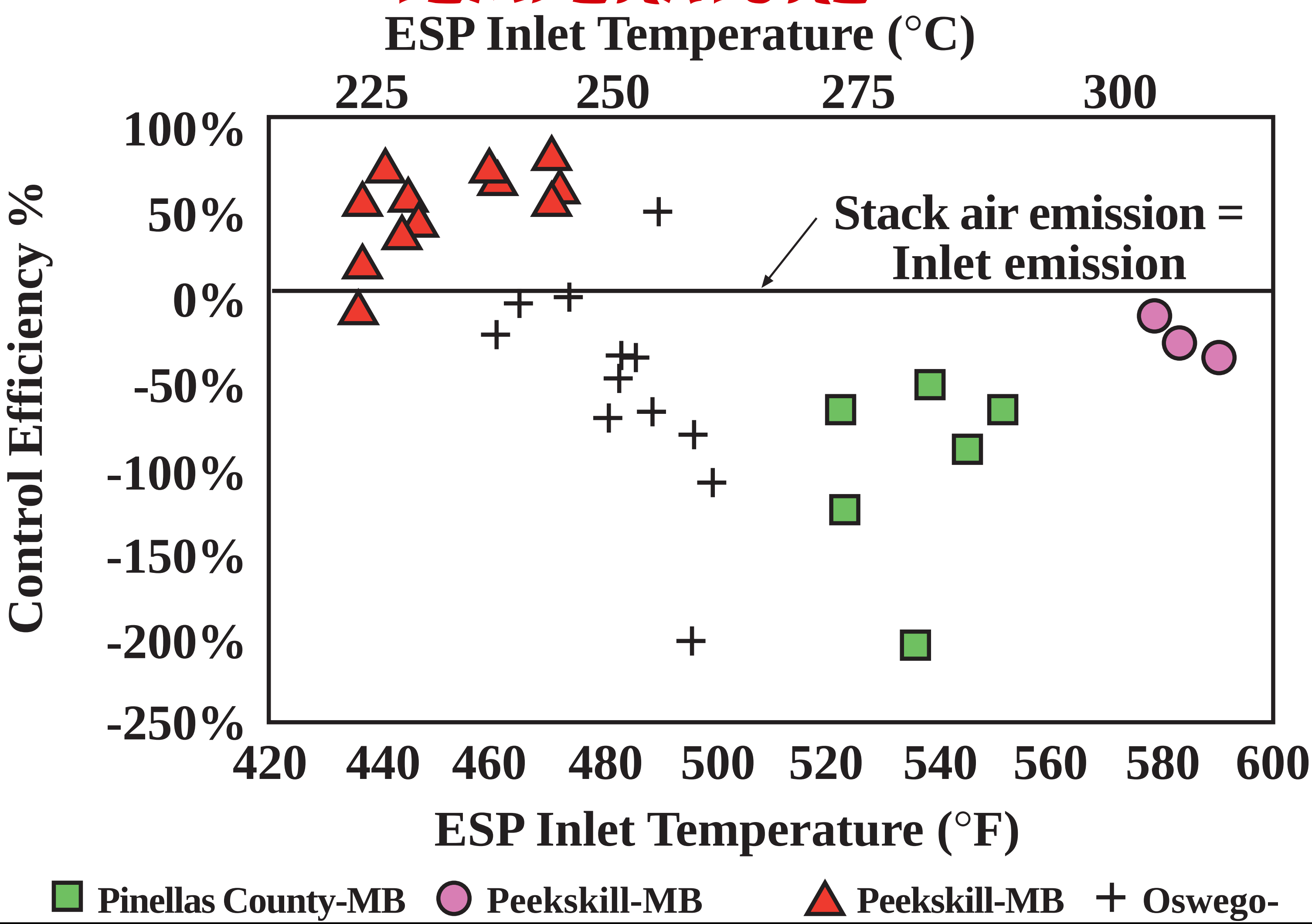


LOW TEMPERATURE FORMATION

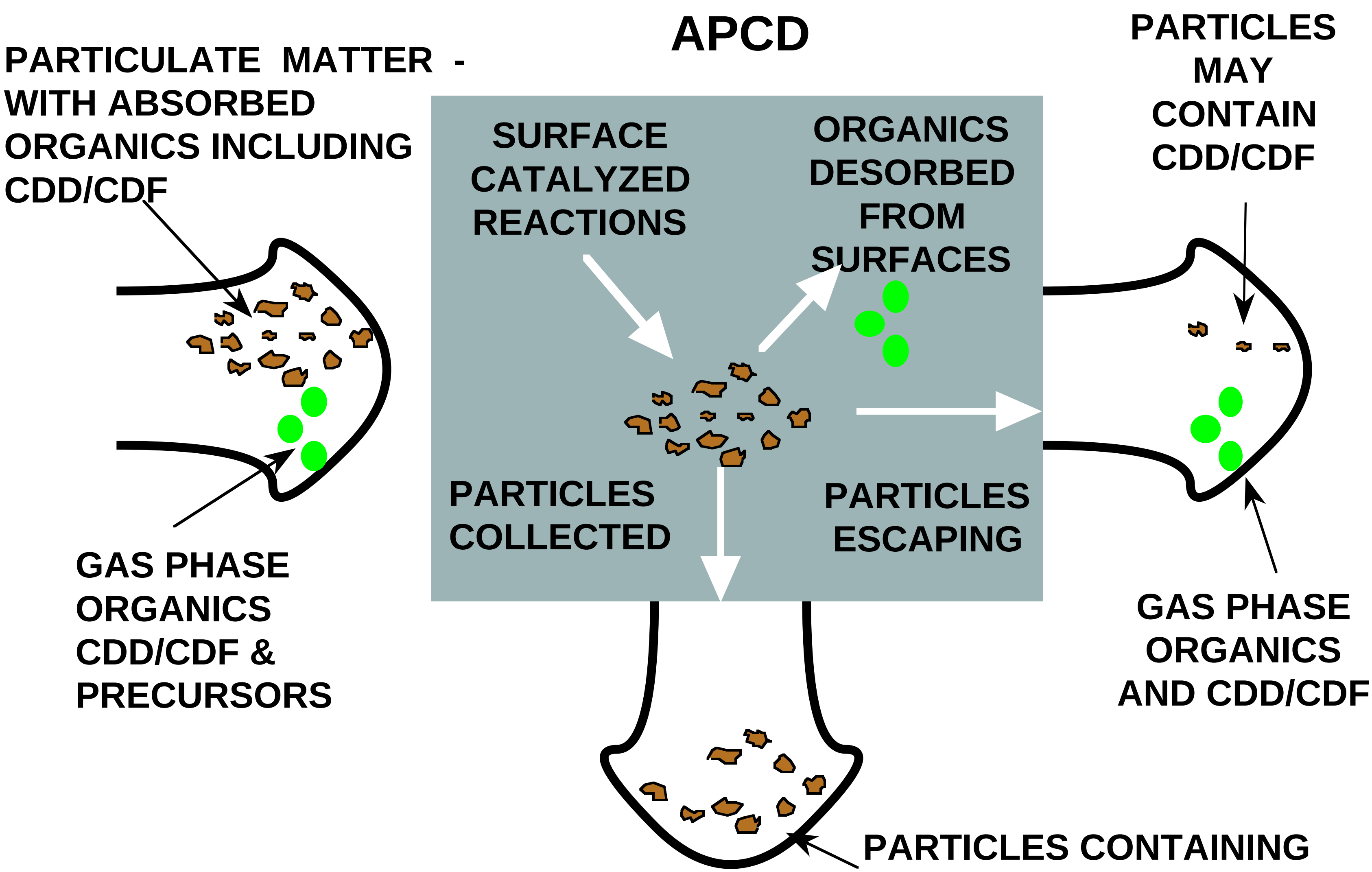
- Data after Swartz et al (1990)



ROLE OF PARTICULATE CAPTURE TEMPERATURE

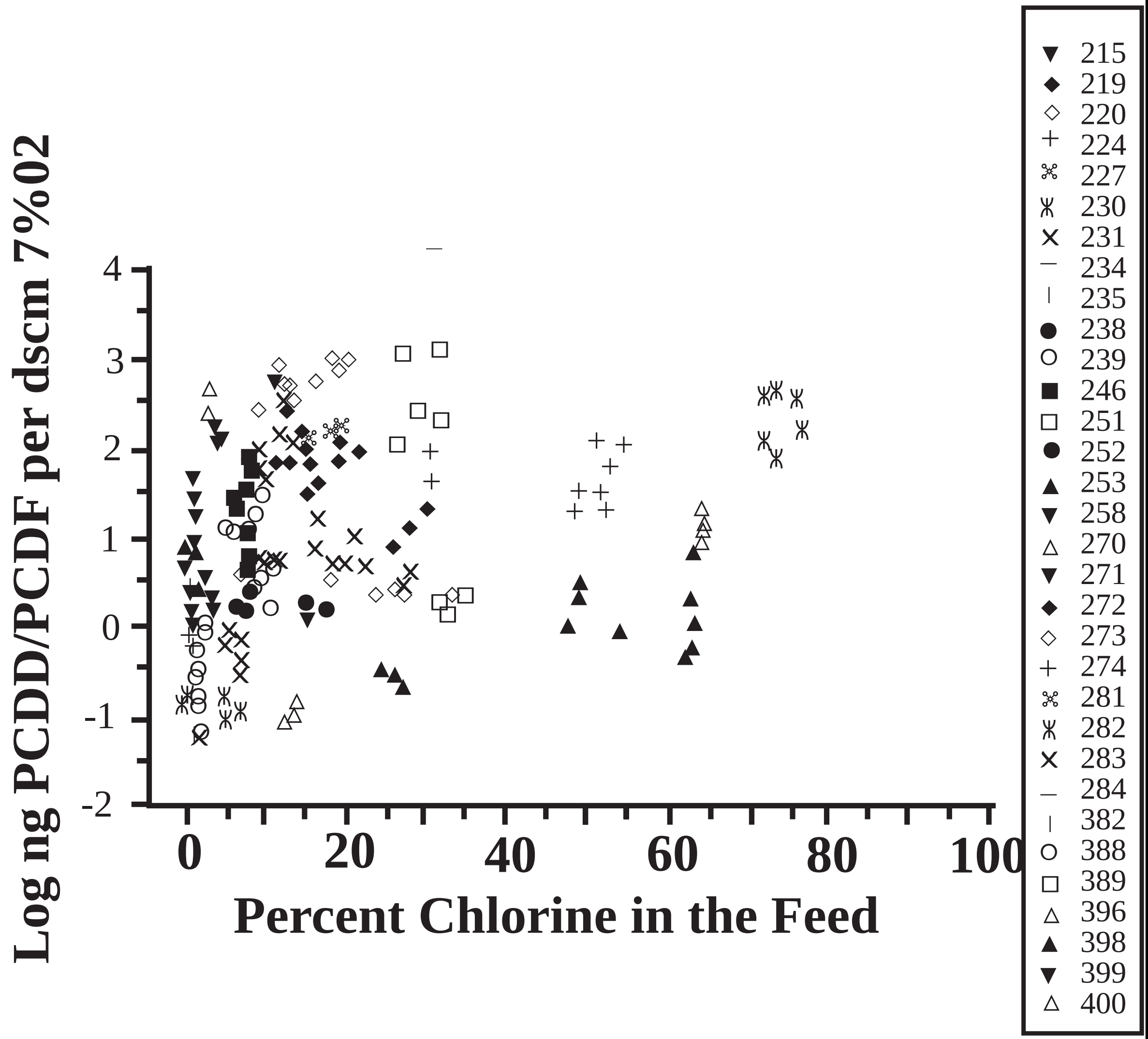


MECHANISMS IN PARTICLE COLLECTION DEVICES



CHLORINE IMPACTS

- **ASME Field Correlations**
  - ***Lack of Relationship between Percent Chloride Feed and Mass of PCDD/F Emitted.***
  - ***Other parameters are controlling***

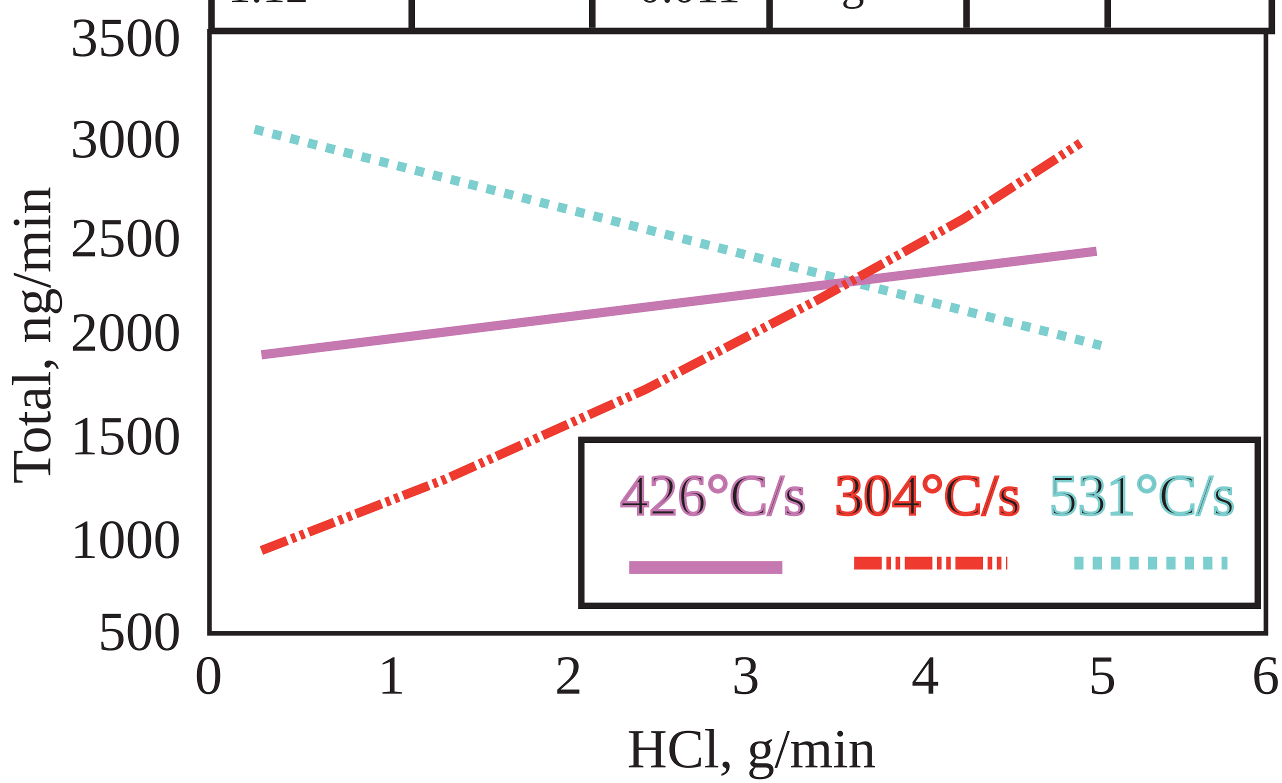


EFFECT OF HCL CONCENTRATION

- Pilot scale RDF data (after Gullett, 1997) indicate that HCl concentration effect is dependent on quench rate

RDF, kg/min	HCl, g/min	SO2, g/min	QU, °C/s	TS, °C	Ca, g/min
1.12	X-Axis	0.011	Legend	338	0

Total PCDD/PCDF



ROLE OF AMBIENT CHLORINE

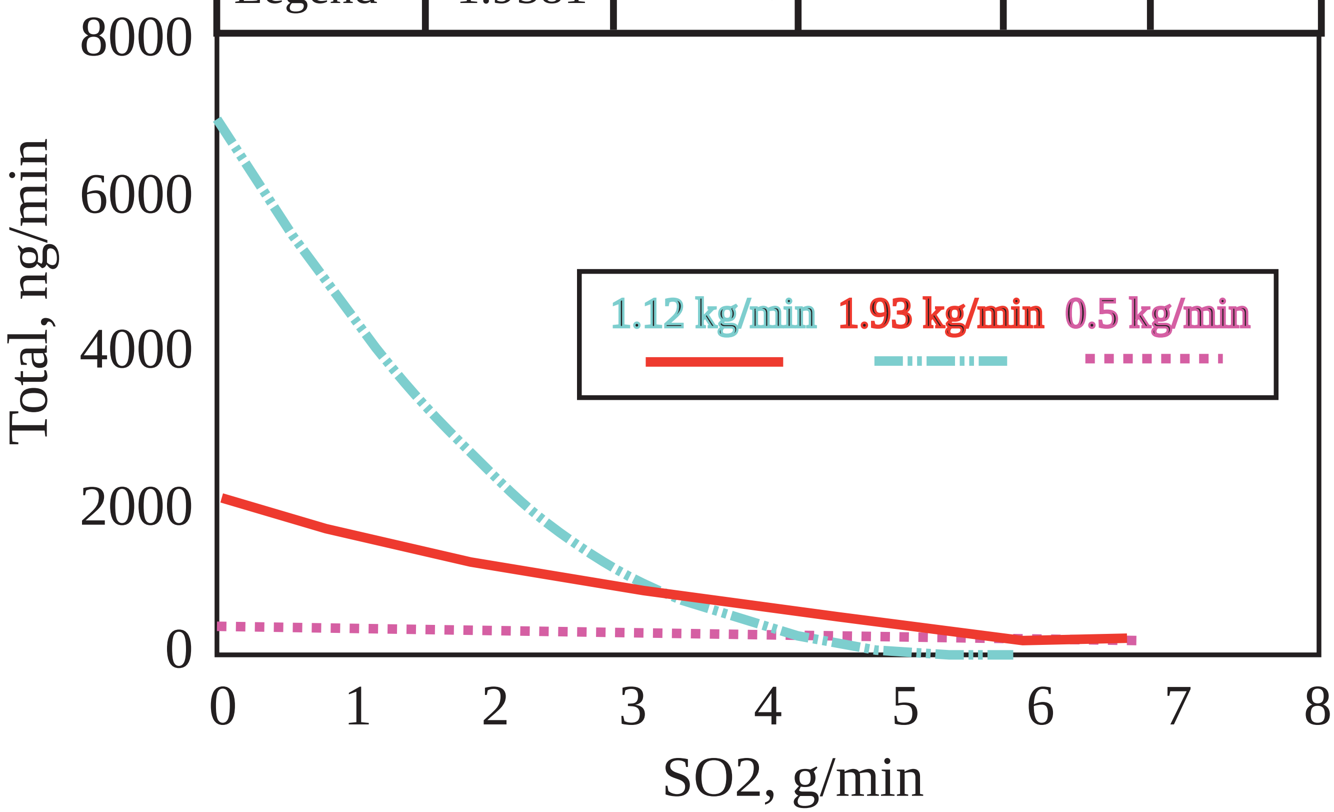
- **Ambient levels of chlorine in atmospheric particulate**
  - *from World Meteorological Organization*
  - *Total global tropospheric Cl concentration*
    - organic bound 3.8 ppb (e.g., long lifetime CFCs, carbon tetrachloride, methylchloroform,)
    - HCl 1.4 ppb
    - particulate bound <0.23 ppb
  - *elevated near coast*
    - some measurements indicate levels of 35 ppb
    - acidification of salt spray
- **Chlorine levels in ambient air (ppb) can be orders of magnitude greater than required to generate ppt levels of PCDD/PCDF**

SULFUR IMPACTS

- Pilot scale RDF data indicate that SO_2 lowers dioxin formation

RDF, kg/min	HCl g/min	SO2, g/min	QU, °C/s	TS, °C	CA, g/min
Legend	1.9581	X-Axis	428	338	0

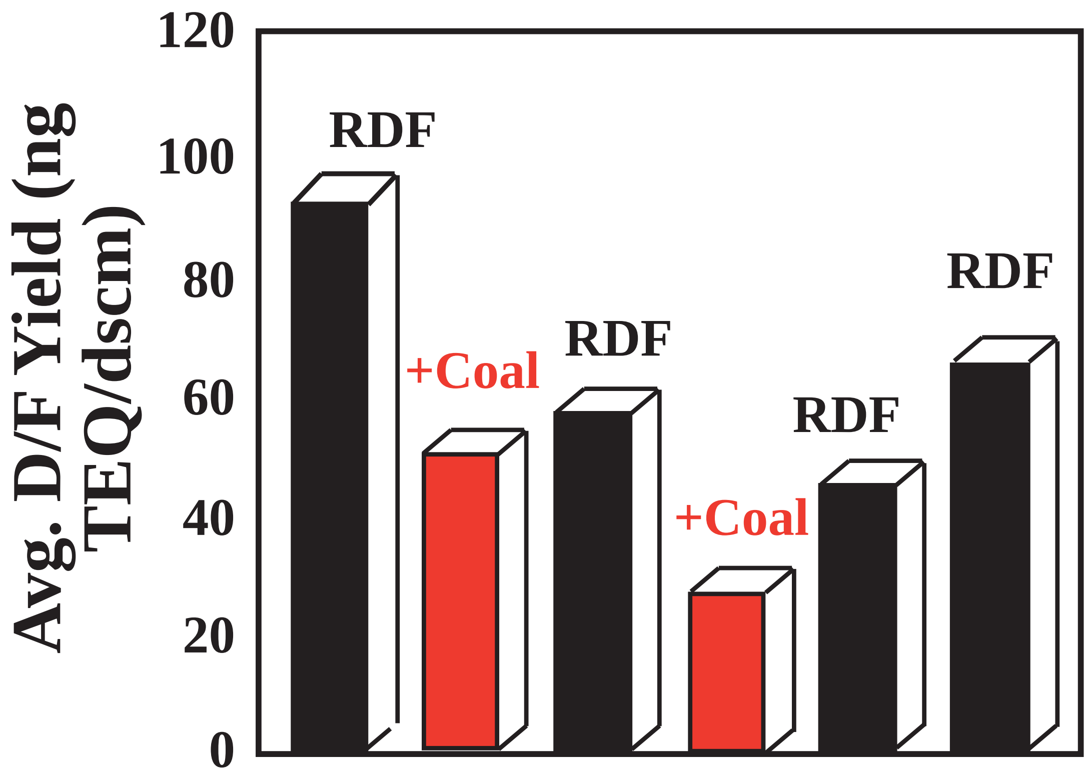
Total PCDD/PCDF



EFFECTS OF COAL COFIRING WITH RDF (EFFECTS OF SULFUR)

- Cofiring of high sulfur coal suppresses RDF's PCDD/PCDF formation (>73%)
- PCDD/PCDF decreases with cofiring cycles, suggesting build up of sulfur effect
- Return to PCDD/PCDF RDF baseline is slow

Full Scale RDF Data prior to APCD
(After Gullett, 1997)



OUTLINE OF TALK

- Structures
- Concentrations of interest
- Measurement Techniques and Issues
- Fundamental Principles
- Dioxin and Furan Formation Chemistry
- **Control Technologies**
- Formation Conditions
- Monitoring Technologies
- Conclusions
- Recommendations

DIOXIN CONTROL

Good Combustion Practice

- *Uniform high temperature*
- *Good mixing with sufficient air*
- *Minimize entrained, unburned particulate matter*
- *Feed rate uniformity*
- *CO and Total Hydrocarbons Emissions as indicators*
- *Temperature at particulate control device*

Air Pollution Control

- *Spray Dryer/fabric filter*
- *Wet Scrubbers*
- *Carbon injection*
- *Carbon beds*
- *Catalysts poisoning agents and inhibitors*
- *Catalytic Oxidations*

CONDITIONS MORE LIKELY TO LEAD TO PCDD/PCDF FORMATION

Listed in Order of Relative Importance

- Poor Combustion Conditions
  - *Mixing, Temperature, Quenches, Transients*
  - *Sooting conditions*
  - *High CO and Total hydrocarbons*
- High particulate entrained from combustion process with poor burnout (high carbon)
- Particulate holdup in critical temperature window (150-450°C)
- Particulate matter which contains metal that can catalyze formation of dioxin
- Waste or fuel with complex organics and/or lignin like structure
- Sufficient Chlorine

CONDITIONS TYPICALLY ASSOCIATED WITH LOW PCDD/PCDF FORMATION

Listed in Order of Relative Importance

- Low Particulate Matter
- Low Temperature or no Particulate Control Device
- Rapid Quenches through dioxin reformation window
- Good Combustion Practice
- Low "catalysts" Metals
- High Sulfur
- Insufficient Chlorine

OUTLINE OF TALK

- Structures
- Concentrations of interest
- Measurement Techniques and Issues
- Fundamental Principles
- Dioxin and Furan Formation Chemistry
- Control Technologies
- Formation Conditions
- **Monitoring Technologies**
- Conclusions
- Recommendations

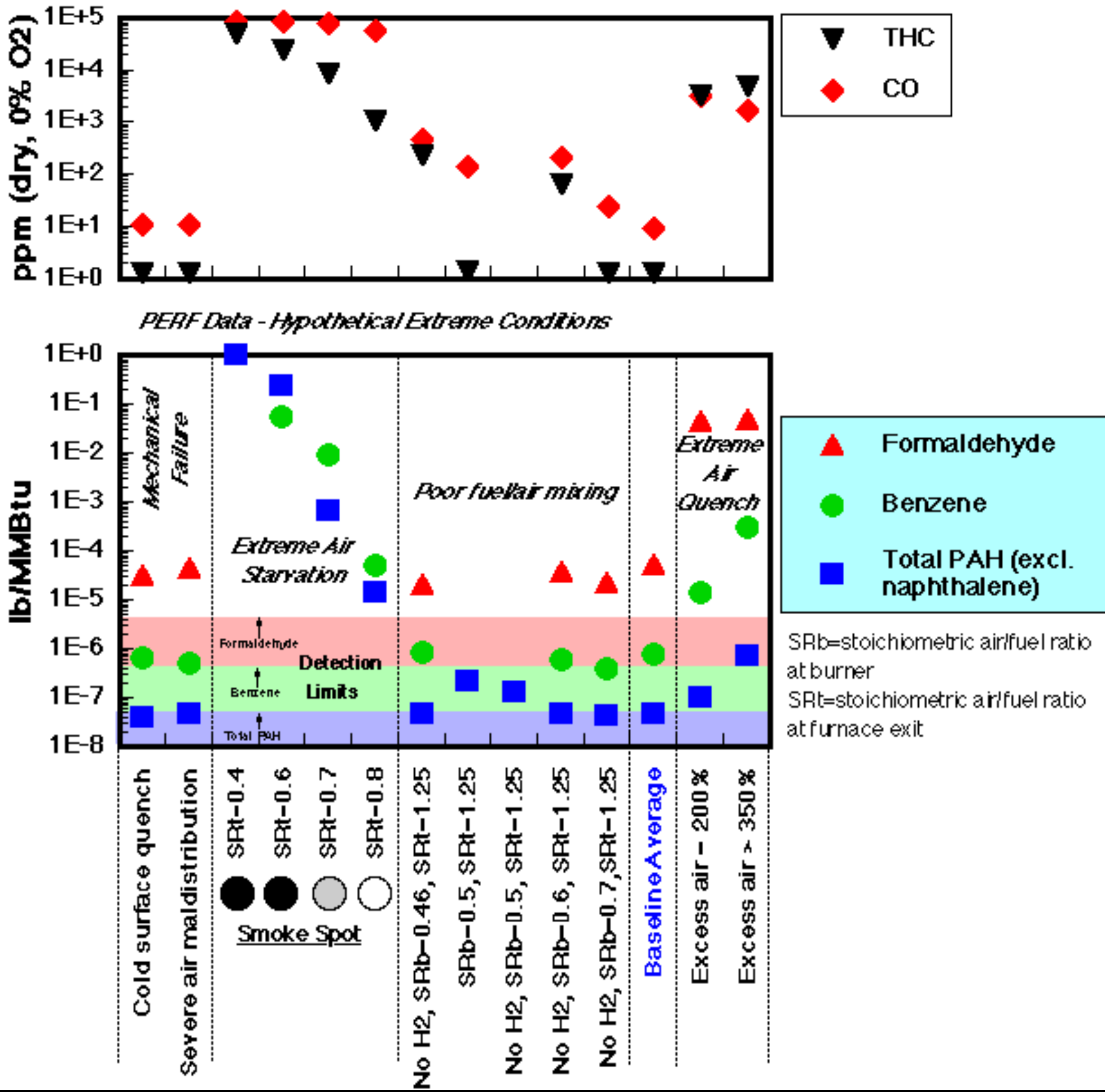
MONITORING AND CONTINUOUS PERFORMANCE ASSURANCE

- **No direct real time monitors exist**
  - *Emerging technologies (REMPI) hold some promise for more direct measurement*
- **Currently must rely on periodic manual sampling and analysis and monitoring of parameters that are known to impact formation and emissions e.g.,**
  - *combustion parameters*
  - *CO/THC indicators of combustion conditions*
  - *PM control device temperature*

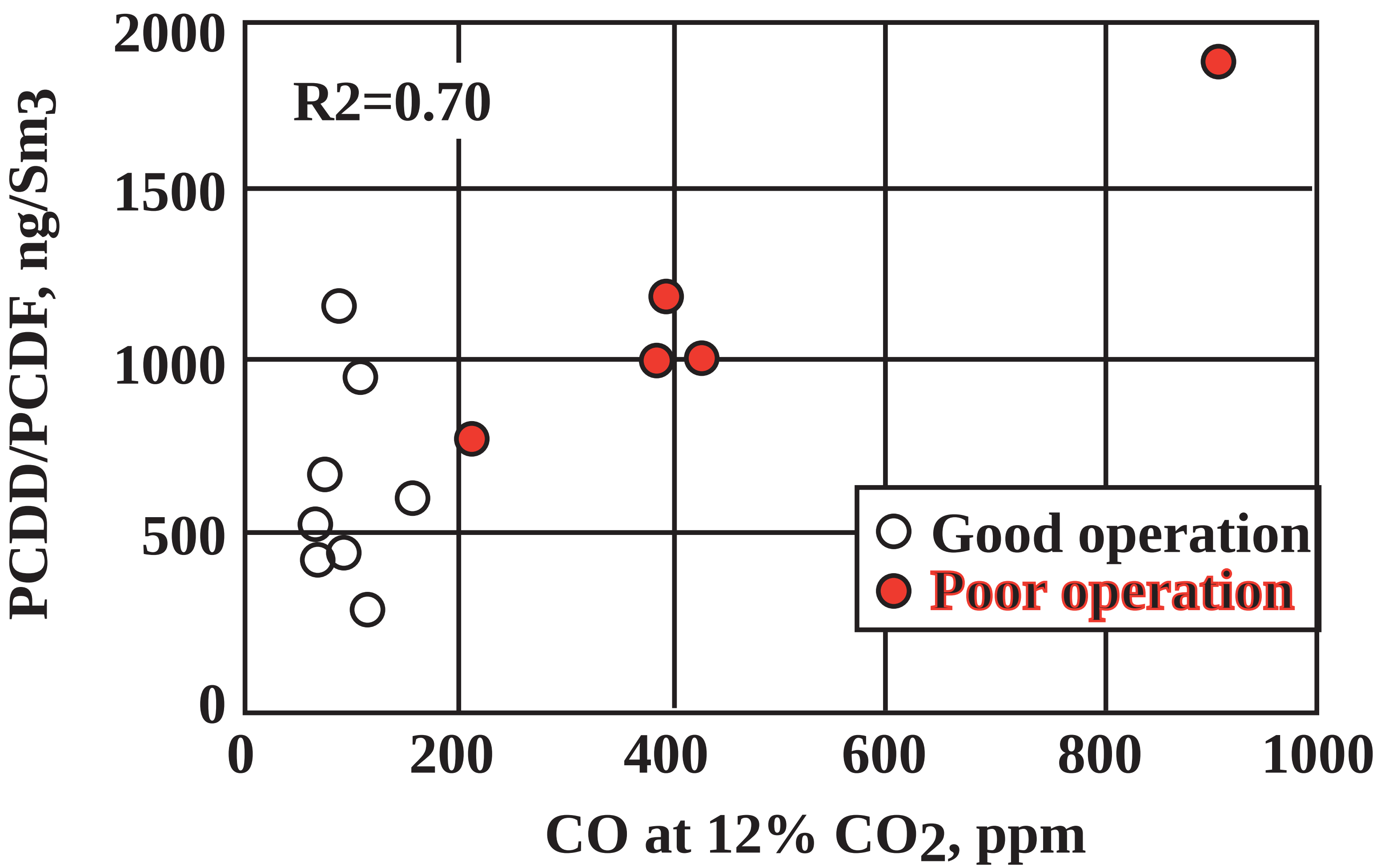
THE USE OF CO AS INDICATOR FOR PCDD/PCDF

- Carbon monoxide is a stable combustion intermediate
- It can be continuously and reliably monitored
- It can be used as an indicator
  - *that conditions are same as compliance tests*
  - *that conditions are good combustion conditions*
- But not as a direct indicator of trace organic emissions

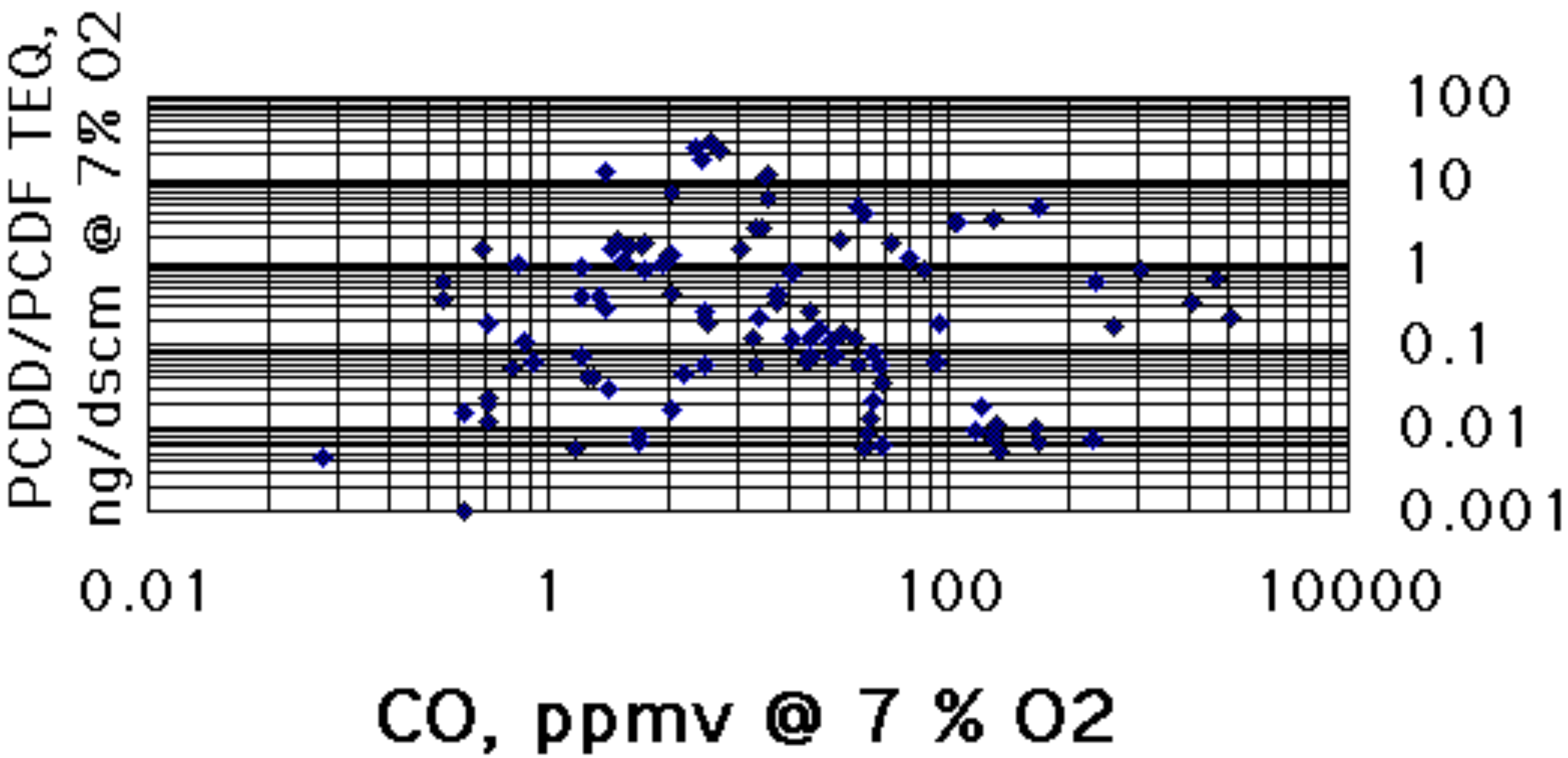
LABORATORY DATA- CO, THC AND HAP



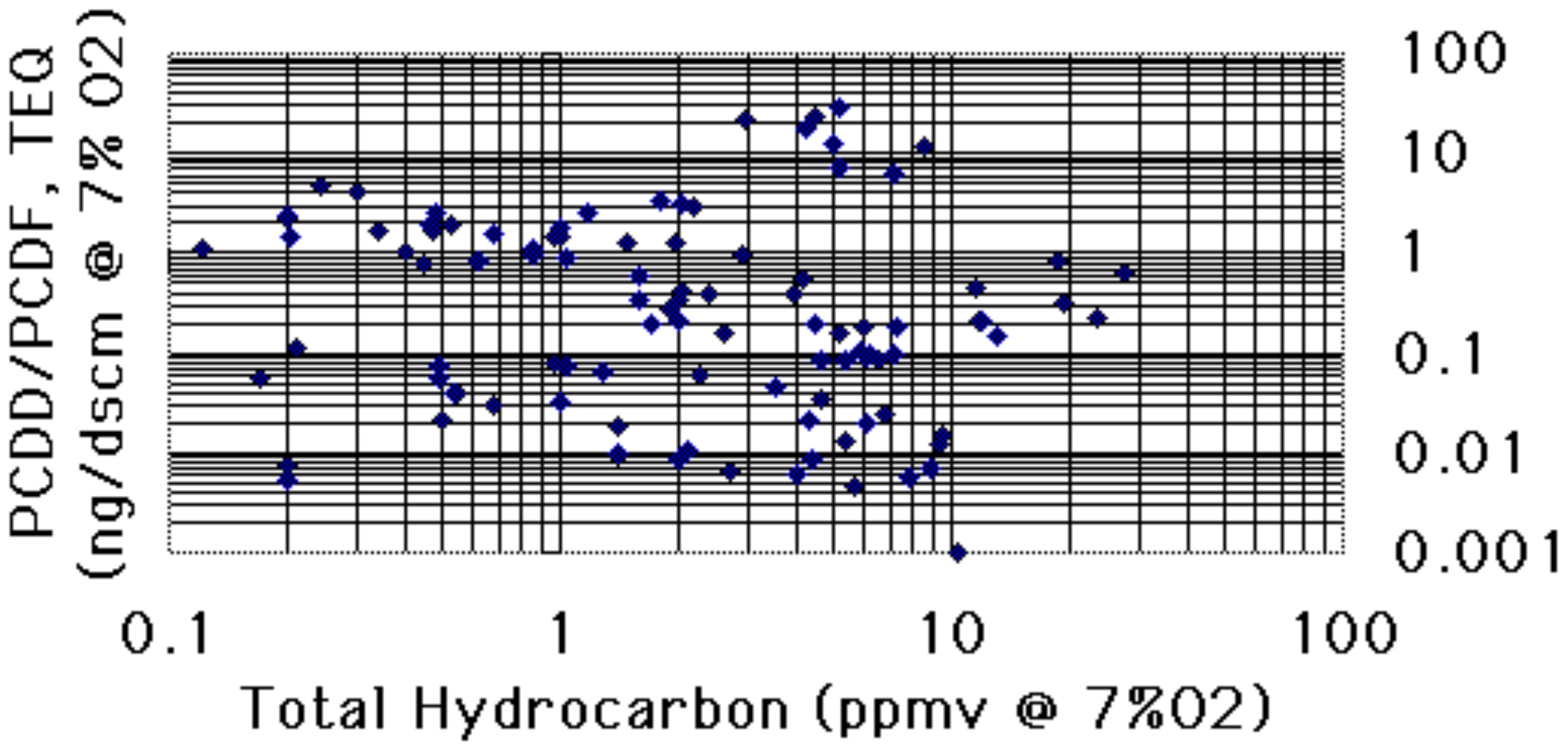
CO AND PCDD/PCDF IN MWCS



CO AND PCDD/PCDF IN HAZARDOUS WASTE INCINERATORS



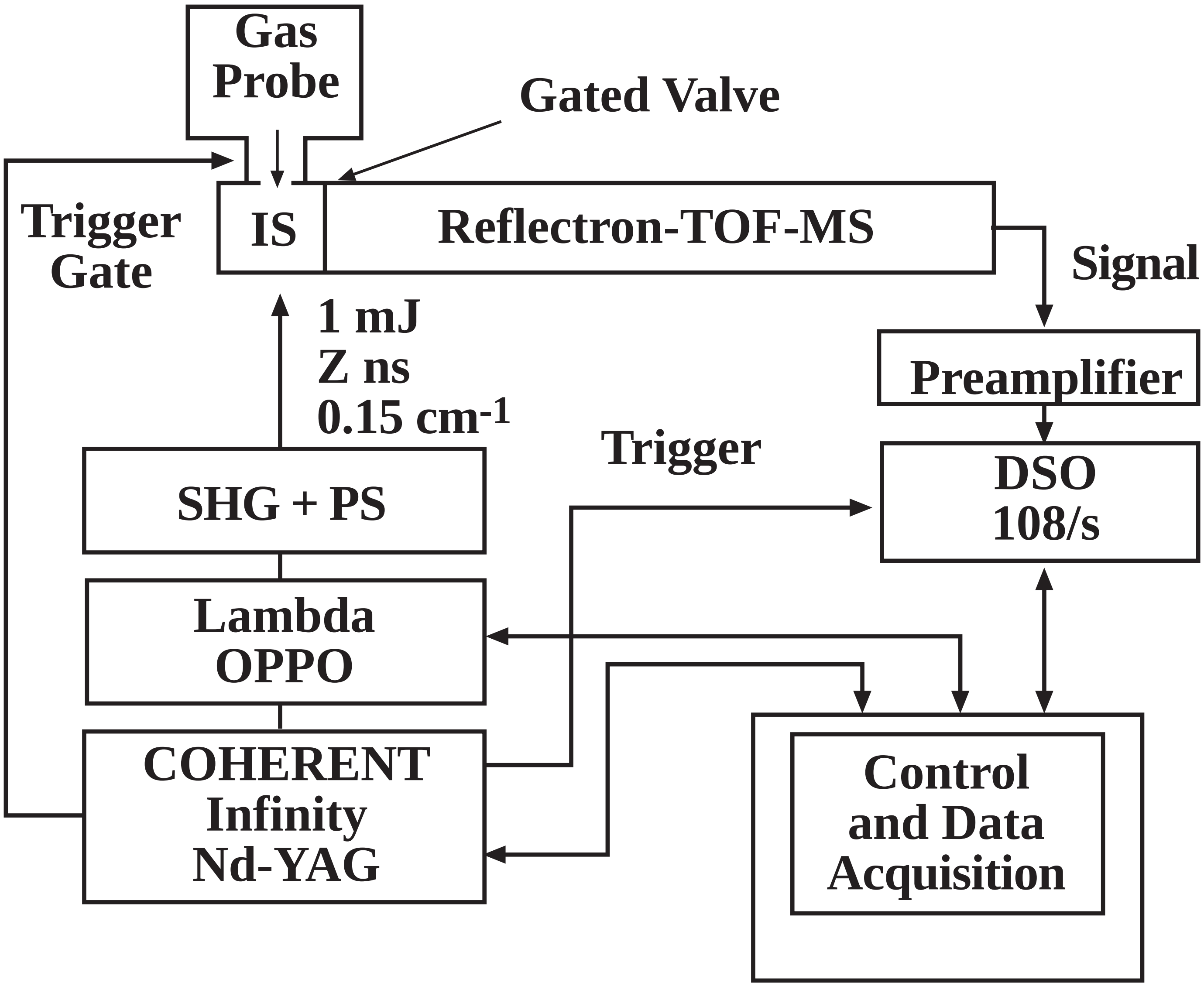
THC AND PCDD/PCDF IN HAZARDOUS WASTE INCINERATORS



ADVANCED MONITORING TECHNIQUES

- Resonance Enhanced Multi-Photon Ionization "REMPI"
- Principles
  - *Molecules have characteristic energies of their intermediate vibrational states*
  - *Selection of laser wavelength in resonance with that vibrational state causes photoionization*
  - *Ionization yields are very high*
  - *Ionization is selective, molecule specific*
  - *Coupled with Time-of-Flight Mass Spectrometer yields 2D analytical tool*

REMPI APPARATUS



CORRELATIONS OF MONO, DI, TRI DIOXINS WITH TEQ

Predictive Models of TEQ with Low Chlorinated Congeners

No. of Isomers	R^2	SS	Variables in Model
1	0.729	66.55	2,3,7-TrCDD
1	0.537	112.501	2,6-DiCDD
1	0.501	122.515	2-MCDF
2	0.736	66.040	2,3,7-TrCDD 2,4-DiCDD
2	0.733	65.377	2-MCDD 2,3,7-TrCDD
2	0.733	65.467	2,3,7-TrCDD 2-MCDF
3	0.767	57.136	2-MCDD 2,3,7-TrCDD 2,4-DiCDF
3	0.760	68.068	2,8-DiCDD 2,3,7-TrCDD 2,4-DiCDF
3	0.757	69.038	2-MCDD 2,3,7-TrCDD 2-MCDF
4	0.770	56.535	2-MCDD 2,3,7-TrCDD 2,4-DiCDF
4	0.769	56.639	2-MCDD 2,8-DiCDD 2,3,7- TrCDD 2,4-DiCDF
4	0.760	58.807	2,8-DiCDD 2,3,7-TrCDD 2-MCDF 2,4-DiCDF
5	0.771	58.189	2-MCDD 2,8-DiCDD 2,3,7-TrCDD 2-MCDF 2,4-DiCDF

CONCLUSIONS

❑ Dioxin levels of interest

- *very low concentrations*
- *difficult to measure*
- *care must be taken when comparing measurements due to differences in measurement and reporting techniques*
- *levels near analytical detection limits and practical quantitation limits*

❑ Monitoring

- *No direct real time monitors exist*
- *Must rely on Parameter monitoring e.g.,*
  - CO/THC indicators of combustion conditions
  - PM control device temperature
- *Emerging technologies (REMPI) hold some promise for more direct measurement*

CONCLUSIONS

Formation Mechanisms

- *Major pathways are defined*
- *Different pathways dominant under different conditions involving both combustion and post combustion regions*
  - **Gas Phase mechanisms**
  - **Solid Phase mechanisms**
- *Kinetics of mechanisms are not established*
  - **Cannot a priori predict PCDD/PCDF formation levels**
- *Key importance of*
  - **Good Combustion Practice**
  - **Particulate matter**
  - **PM control Device Temperature**

CONDITIONS MORE LIKELY TO LEAD TO PCDD/PCDF FORMATION

- Poor Combustion Conditions
  - *Mixing, Temperature, Quenches, Transients*
  - *Sooting conditions*
  - *High CO and Total hydrocarbons*
- High particulate entrained from combustion process with poor burnout (high carbon)
- Particulate holdup in critical temperature window (150-450°C)
- Particulate matter which contains metal that can catalyze formation of dioxin
- Waste or fuel with complex organics and/or lignin like structure
- Sufficient Chlorine

RECOMMENDATIONS

- Examine source design and operation for conditions potentially favoring dioxin formation
- Examine existing dioxin emissions data bases for similar sources
- Support research leading to screening and predictive models for PCDD/PCDF from practical combustion systems
- Field test on sources
  - *If funds limited focus on more likely sources based upon current understanding of PCDD/PCDF mechanisms*
  - *Data collection should include parameters known to influence PCDD/PCDF formation and control*
  - *Data engineering analysis to interpret and generalize to other configurations*
  - *Address practical quantitation limit*
- Emphasis on continuous performance assurance and advanced monitoring techniques

TESTING RECOMMENDATIONS

Source	Fuel	Potential	Rationale/parameters
Incinerators	Waste	High	Complex organic, Entrained PM, PM Control, metals & Cl, PM Control Temp
Boilers	Wood/biomass	Mod-High	Complex Organics, entrained PM, PM control, Cl, Metals, PM Control Temp
Boilers	Landfill gas	Moderate	Transients, Complex HC, Cl, Low PM
Boilers	Residual Oil	Mod-Low	Sooting, metals, S/Cl, PM control Temp
IC Engines	Landfill gas	Moderate	Transients, Complex HC, Cl, Low PM
Boilers	Coal	Low-mod	S/Cl ratio, GCP, Entrained PM, PM Control, C in ash, metals
Heaters	Process gas	Low	GCP, transients, potential catalysts, low PM
Flares	Waste Gas	Low	No PM control, rapid quench
Boilers	Distillate Oil	Low	Sulfur, GCP, low Cl
IC Engines	Diesel	Low	PM present,Low Cl, Temp Profile
Turbines	Distillate Oil	Low	GCP, no PM control, thermal quench
Boilers	Natural Gas	Very Low	GCP, very low PM, Low metals andCl
IC Engines	Natural Gas	Very Low	Very low PM, GCP, Low metals and Cl
Turbines	Natural Gas	Very Low	GCP, very low PM, Rapid Quench, Low metals and Cl