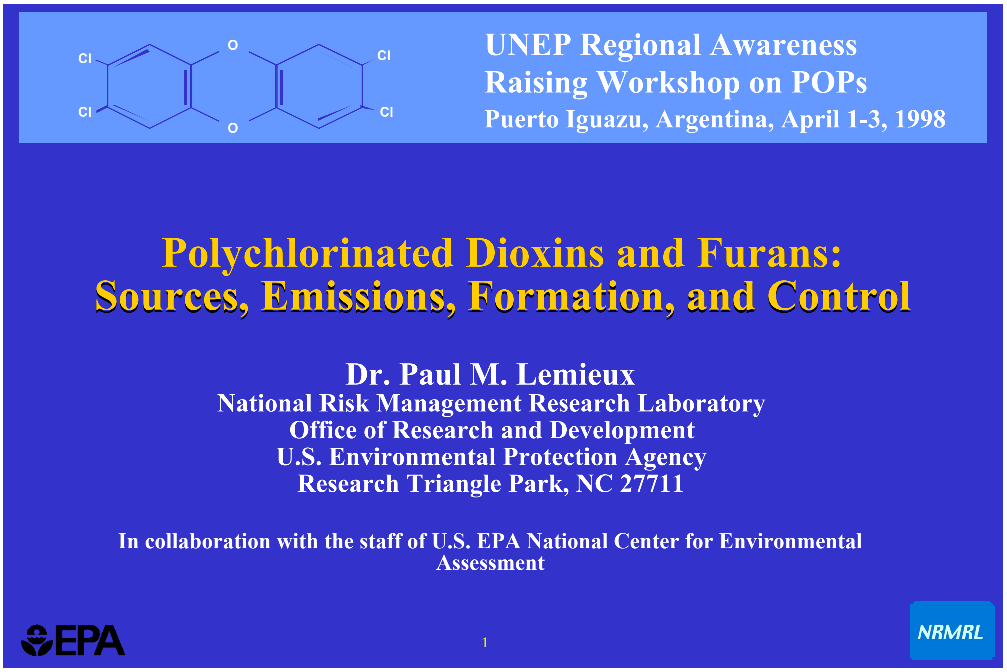


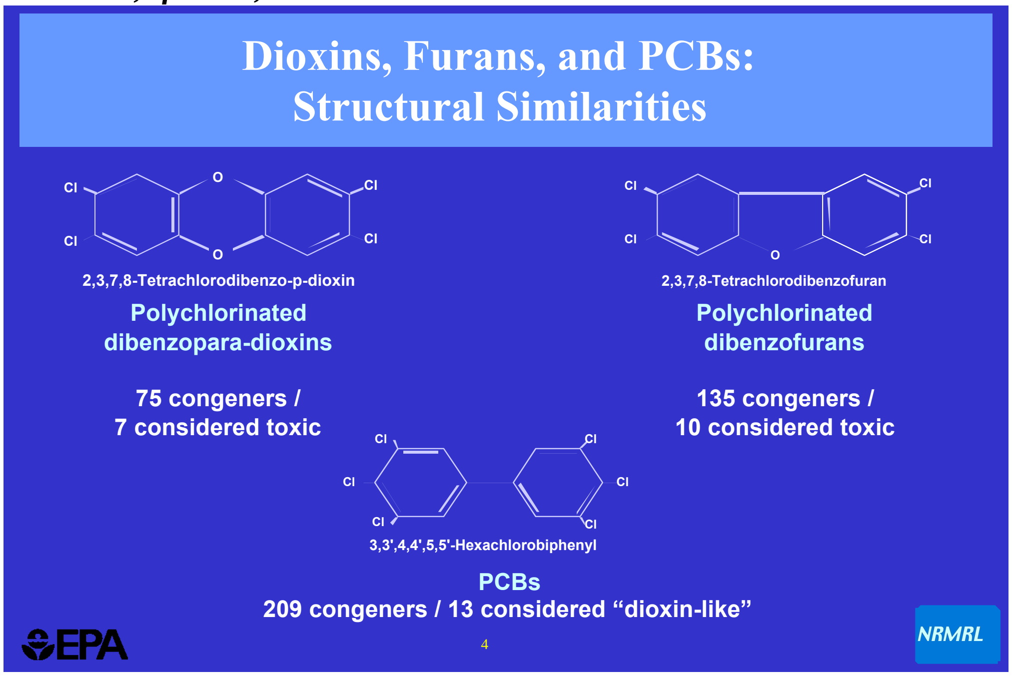
Polychlorinated Dioxins and Furans: Sources, Emissions, Formation, and Control

Presentation to UNEP Regional Awareness Raising Workshops on POPs: Iguazu, Argentina, April 1-3, 1998

Dr. Paul M. Lemieux

Thank you for allowing me the opportunity to present an outline of work performed by the United States Environmental Protection Agency (EPA) on sources, emissions, formation, and control of polychlorinated dioxins and furans. I trust that this presentation will serve as an introduction to the scientific information and terminology used in the risk assessment and risk management of dioxins and dioxin-like chemicals. The text of the presentation is formatted to be read in conjunction with the accompanying slides, which are indicated by sequence number and title. The presentation covers the chemical structure of these chemicals; a brief note on how they affect humans; the concept of toxicity equivalence; emission sources in the United States; measurement techniques; formation mechanisms; exposure routes; and control schemes. Should additional information be desired on any of these topics, the EPA Internet site (http://www.epa.gov/) offers a valuable resource where work products from the dioxin reassessment and other United States regulatory activities are posted for public dissemination. Note that my main area of expertise lies in the combustion research area dealing with pollutant formation and control. I wish to acknowledge my colleagues at the EPA National Center for Environmental Assessment for their input on the exposure and health related aspects of this presentation.

Slide 4: Dioxins, furans, and PCBs: structural similarities

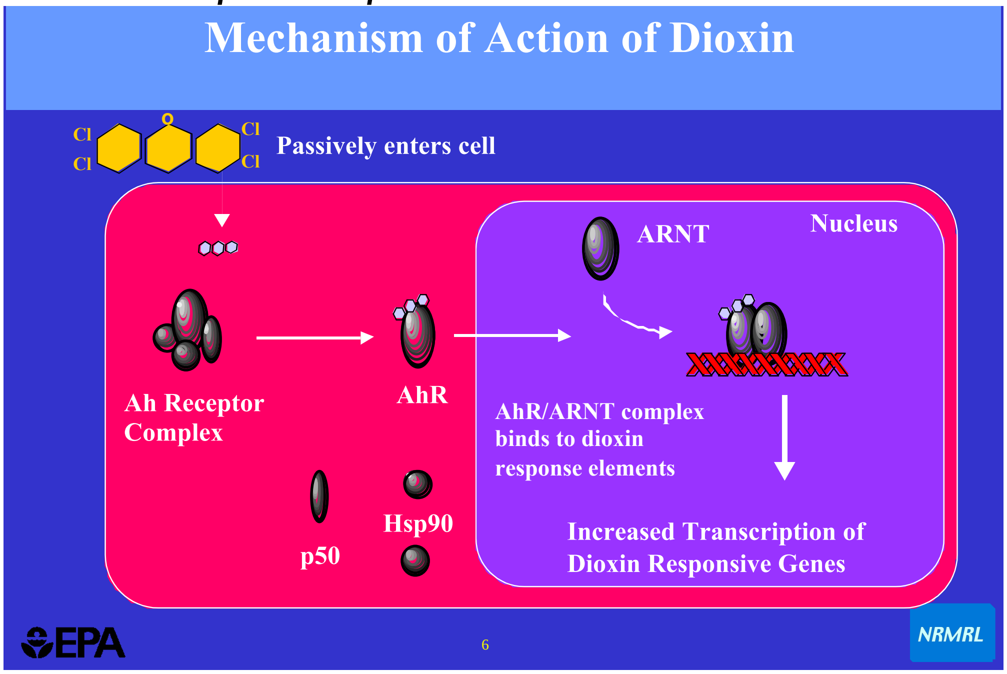


The structure of dioxins, furans, and PCBs warrants special consideration, as it is the specific shape of the molecules and attached chlorine atoms that governs their toxicity. Dioxin is the abbreviated, common, name for the 75 chemicals comprising the family of polychlorinated dibenzopara-dioxins (PCDDs). The most toxic of the dioxin molecules, 2,3,7,8-tetrachlorodibenzo-p-dioxin, is depicted in the upper left of slide 4. All dioxin molecules have in common two benzene rings joined by two oxygen molecules (di-oxin). Varying numbers of chlorine atoms (up to eight) can be located at different positions around this structure, resulting in 75 different structural configurations known as congeners. Note the flat, planar structure of this molecule and the symmetrical location of the chlorine atoms at the far ends. Seven of the PCDD congeners are considered to exhibit "dioxin-like" toxicity, resulting from the structural configuration of the chlorine atoms.

Furans are depicted in the upper right corner of slide 4, the specific example being 2,3,7,8-tetrachlorodibenzofuran. Polychlorinated dibenzofurans (PCDFs) differ structurally from PCDDs only by a carbon-carbon bond substituting for one of the oxygen bonds. Differing possible arrangements of chlorine atoms around the dibenzofuran molecule give rise to 135 congeners, of which 10 are considered to exhibit toxic, "dioxin-like," properties.

Polychlorinated biphenyls (PCBs) are depicted at the bottom of slide 4. A critical difference between PCBs and the PCDD/PCDFs is the ability of the PCB to rotate around the single bond connecting the benzene rings. This rotation occurs principally when there are one or more chlorine atoms located near the connecting bond, in what is known as the "ortho" position. Rotation within the PCB molecule causes a loss of the flat, planar, shape, thereby reducing its potential to exhibit "dioxin-like" properties. Of the 209 PCB congeners, 13 are thought to exhibit "dioxin-like" toxicity.

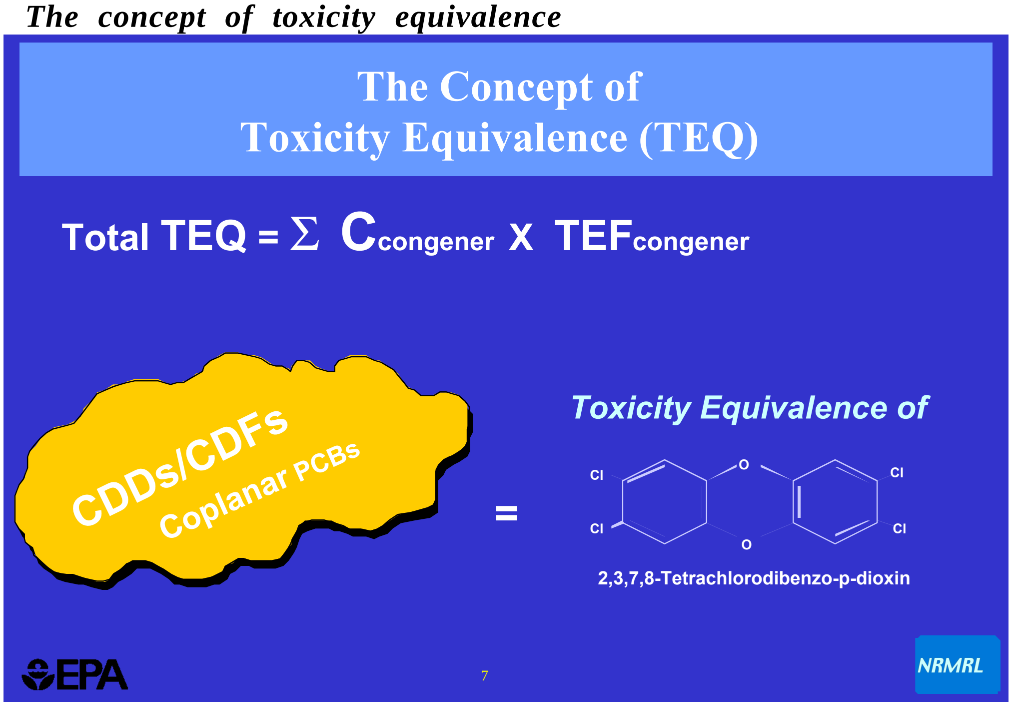
Slide 6: Mechanism of action of dioxin



Integral to an understanding of the toxicity of dioxin-like agents is their ability to bind to the aryl hydrocarbon (Ah) hydroxylase receptor, transport to the cell nucleus, and directly increase the transcription of dioxin responsive genes. The strength of binding by the respective PCDDs, PCDFs, and coplanar PCBs to the Ah receptor correlates with their ability to induce DNA transcription. This is the foundation for the toxicity equivalence factors (TEFs; slides 7 & 8). The receptor-based mechanism and ability to disrupt cellular processes are the basis for the exquisite toxicity of dioxin-like substances to certain species.

Other proteins noted on this diagram are the 90 kiloDalton heat-shock protein (Hsp90), an accompanying 50 kiloDalton protein (p50), and the Ah-receptor nuclear transferase (ARNT) protein.

Slide 7: The concept of toxicity equivalence



You will have noted from the above discussion that a total of 30 PCDDs, PCDFs, and PCBs are currently considered to exhibit dioxin-like toxicity. This raises a problem for toxicity assessments where measurements detect various levels of the different PCDD/PCDF/PCB congeners, each of which has a different potential to elicit dioxin-like effects. Rather than perform 30 individual assessments, scientists have developed the concept of toxicity equivalence to sum the effects of dioxin-like chemicals. Each congener is given a toxicity equivalence factor (TEF) based on its specific ability to elicit dioxin-like effects. The congener 2,3,7,8-tetrachlorodibenzo-p-dioxin (slide 4, upper left) is the most toxic congener and is given a TEF of 1. Other congeners are given TEFs that are fractions of 1. The total toxic equivalent quantity (TEQ) is the sum of all the individual PCDD/PCDF/PCB concentrations multiplied by their specific TEFs.

A word of caution is necessary here: there are a number of different units for reporting dioxin measurements. It is important to be aware of the specific unit in use when comparing studies and between exposures and toxic effects. Measurement units can include:

- -- levels of individual congeners, particularly 2,3,7,8-TCDD;
- -- TEQs based on dioxins only;
- -- TEQs based on dioxins and furans;
- -- TEQs based on dioxins, furans, and coplanar PCBs;
- -- total dioxins, not adjusted to TEQs; and
- -- calculations based on different TEF values.

Slide 8: Dioxin-like compounds and toxicity equivalence factors

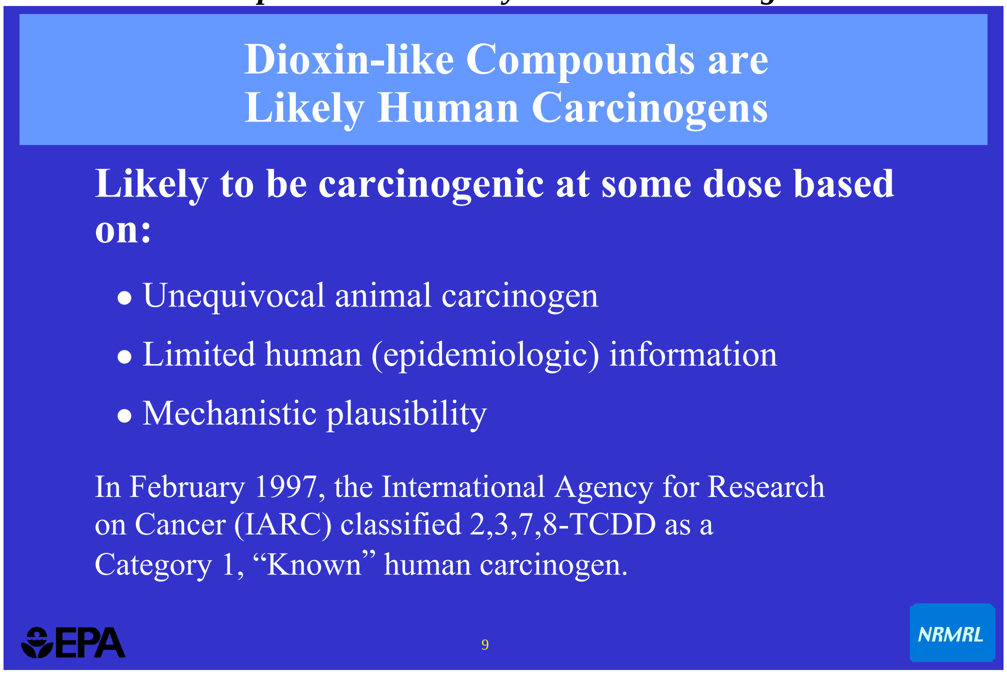
Dioxin-Like Compounds and Toxicity Equivalence Factors

CDD Congener	TEF	CDF Congener	TEF	Coplanar PCB (IUPAC #)	TEF
2378- TCDD	1.0	2378- TCDF	0.1	(77) 3,3',4,4'- TCB	0.0005
12378- PeCDD	0.5	12378- PeCDF	0.05	(126)3,3',4,4',5- PeCB	0.1
123478- HxCDD	0.1	23478- PeCDF	0.5	(169)3,3',4,4',5,5'- HxCB	0.01
123678- HxCDD	0.1	123478- HxCDF	0.1	(105)2,3,3',4,4'- PeCB	0.0001
123789- HxCDD	0.1	123678- HxCDF	0.1	(118)2,3',4,4',5- PeCB	0.0001
1234678- HpCDD	0.01	123789- HxCDF	0.1	(123)2',3,4,4',5- PeCB	0.0001
12346789- OCDD	0.001	234678- HxCDF	0.1	(156)2,3,3',4,4',5- HxCB	0.0005
		1234678- HpCDF	0.01	(157)2,3,3',4,4'5'- HxCB	0.0005
		1234789- HpCDF	0.01	(167)2,3',4,4',5,5'- HxCB	0.00001
		12346789- OCDF	0.001	(114)2,3,4,4',5- PeCB	0.0005
				(170)2,2',3,3',4,4',5- HpCB	0.0001
				(180)2,2',3,4,4',5,5'- HpCB	0.00001
				(189)2,3,3',4,4',5,5'- HpCB	0.0001
Total TetraCDD		Total TetraCDF			
Total PentaCDD		Total PentaCDF			
Total HexaCDD		Total HexaCDF			
Total HeptaCDD		Total HeptaCDF			
Total PCDD		Total PCDF			

EPA 8 NRMRL

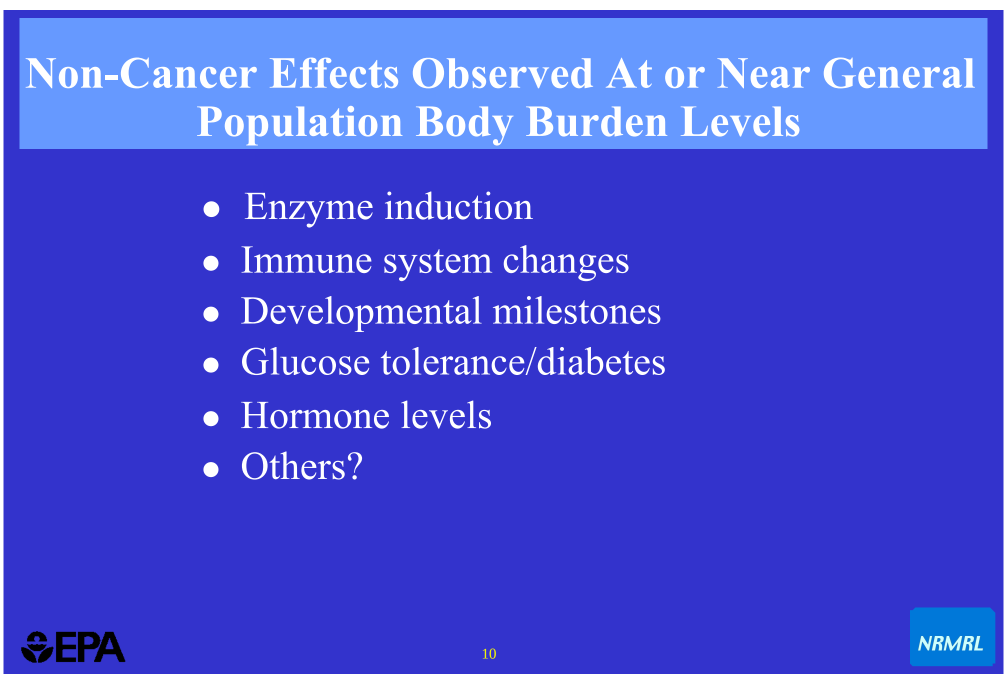
This table provides the list of the current TEF values in use by the U.S. EPA for human health assessments.

Slide 9: Dioxin-like compounds are likely human carcinogens



In February, 1997, the International Agency for Research on Cancer (IARC) classified 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) as a category 1, "known" human carcinogen. The decision that 2,3,7,8-TCDD was likely to be carcinogenic to humans at some dose was based on: unequivocal animal bioassay evidence of carcinogenicity; limited human, epidemiological, information from occupational and other exposures; plus mechanistic plausibility.

Slide 10: Non-cancer effects observed at or near general population body burden levels



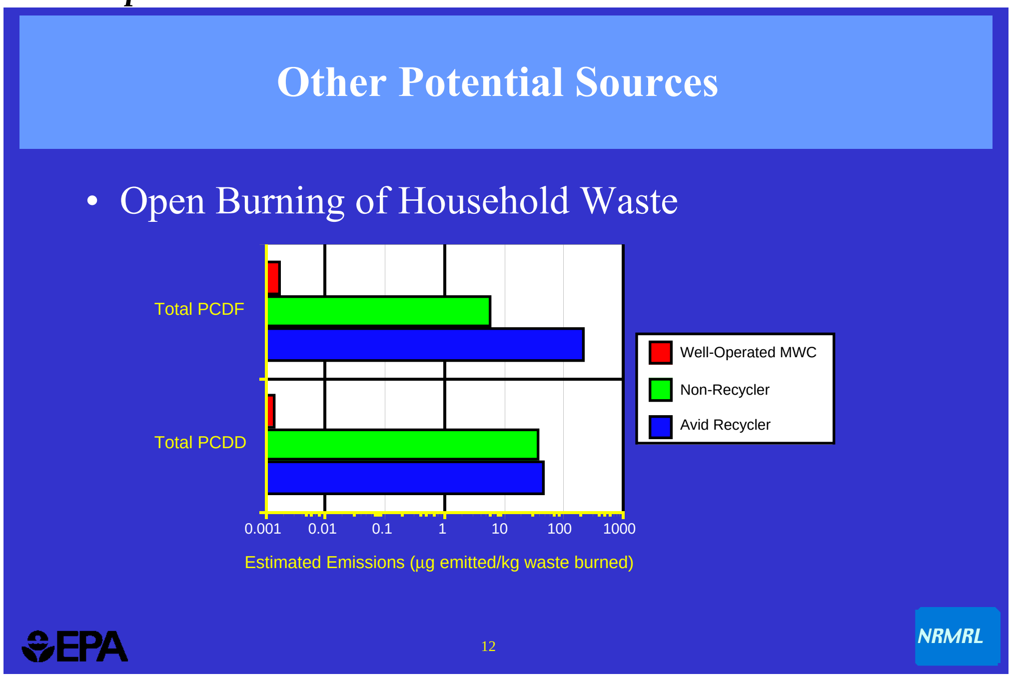
The following dioxin-related effects have been observed at or near general U.S. population body burden levels:

-- enzyme induction;

-- immune system changes;
-- development milestone changes;
-- glucose tolerance changes;
-- altered hormone levels, etc.

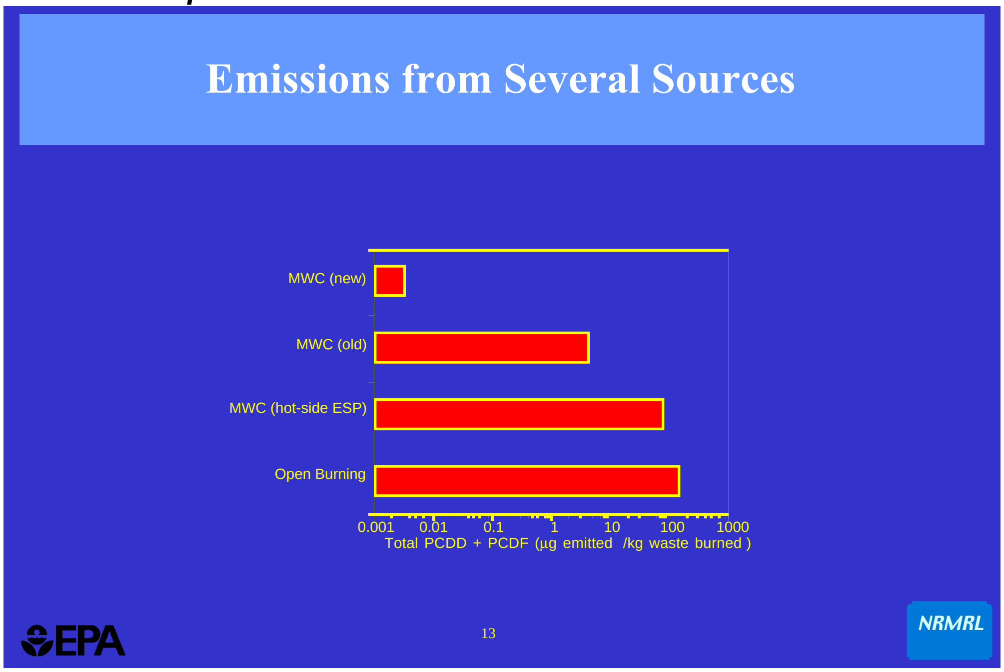
These effects are generally considered to be adaptive changes, but have the potential to be adverse.

Slide 12: Other potential sources



There are a number of sources for which only very limited data exist on emission of dioxins and furans. One such source, the emissions from which were only recently published, is open burning of household waste in barrels. Many rural areas of the United States do not have access to a central facility for waste management, and some of the waste gets burned in barrels by the homeowner. The poor combustion conditions present in this type of combustion, coupled with the plume temperatures that are ideally suited for formation of dioxins and furans, result in very high potential emissions. The limited data that are available indicate that a single household burning its garbage in barrels can produce daily emissions of dioxins and furans on the same order of magnitude as a well-operated municipal waste incinerator that serves tens of thousands of households. This has potential impact in developing countries, where this practice may be more widespread.

Slide 13: Emissions from several sources

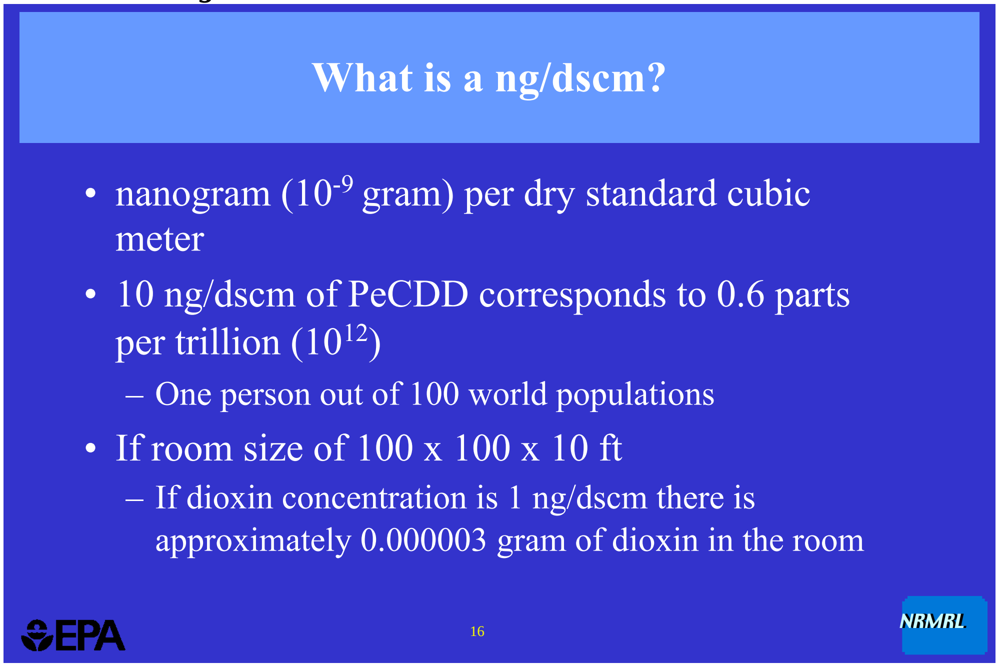


As a perspective showing the wide range of possible emissions from burning essentially the same material, this graph shows, in units of µg total PCDD+PCDF per kilogram of waste burned, emissions from: open burning; combustion in a municipal solid waste combustor with the electrostatic precipitator (ESP) operated at a temperature conducive to formation of dioxins and furans; combustion in an older municipal solid waste combustor; and combustion in a newer municipal solid waste combustor operating within current U.S. regulatory limits.

Slide 14: Current U.S. dioxin standards

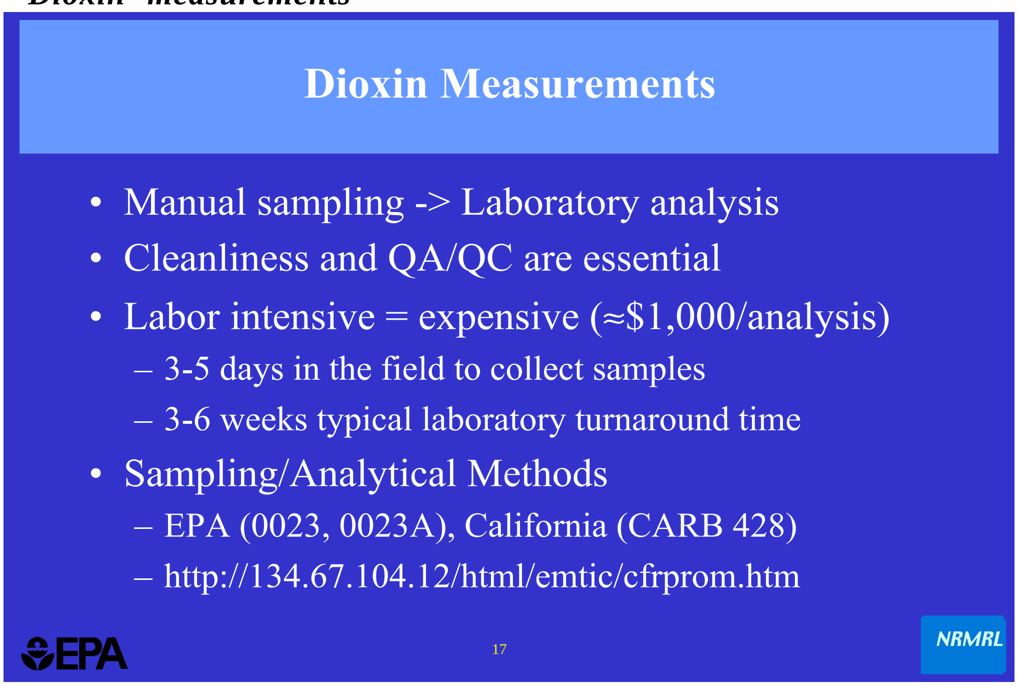
This slide lists the current or proposed emission standards for various combustion devices that can emit dioxins.

Slide 16: What is a ng/dscm?



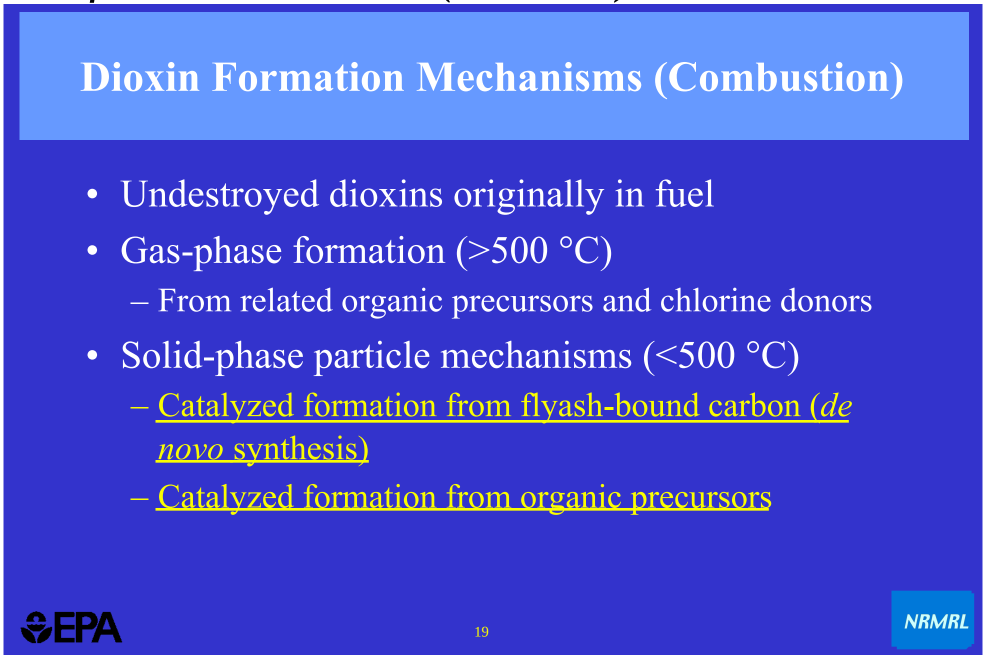
This slide gives some perspective as to the levels at which dioxins and furans are emitted from combustion devices. This will give insight to why sampling and analysis is so expensive.

Slide 17: Dioxin measurements



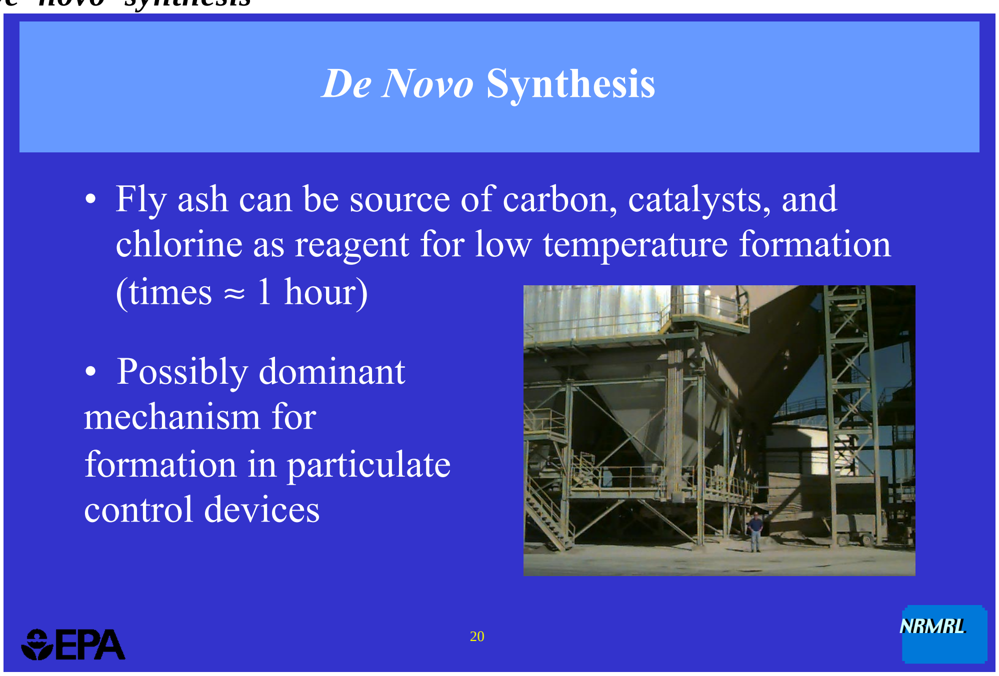
This slide describes how dioxins are measured from stack gases. The high degree of quality assurance needed, coupled with the labor intensity of the analysis, leads to a high cost per sample. The Internet address for the various EPA sampling methods is also given.

Slide 19: Dioxin formation mechanisms (combustion)



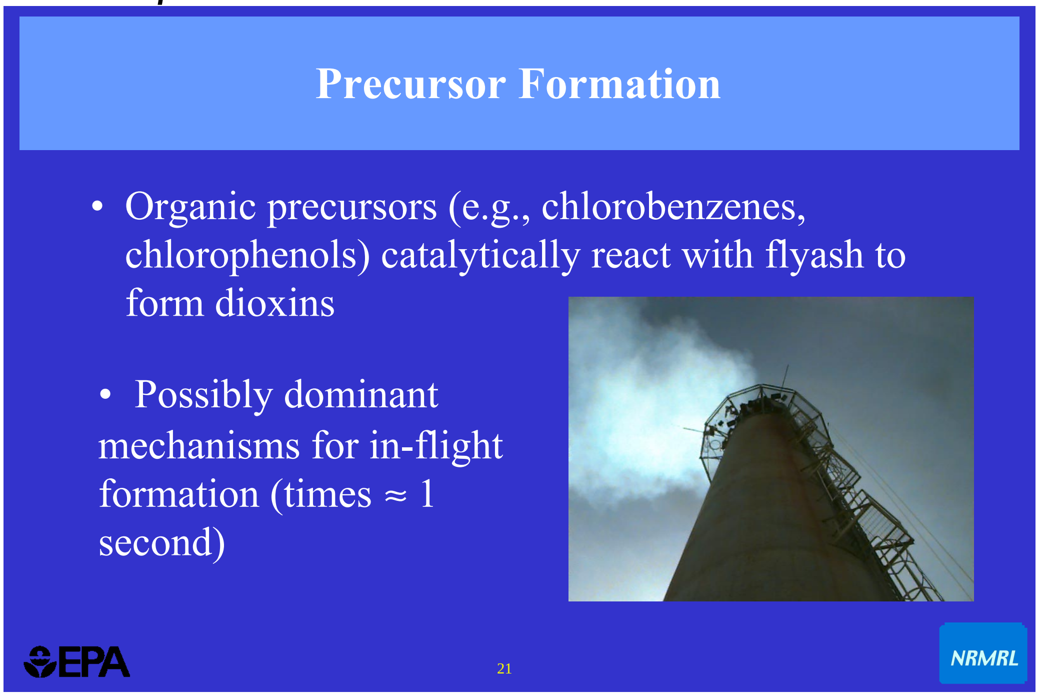
This slide describes the three ways which can lead to emission of dioxin from a combustion device. The two mechanisms that are predominant from incineration sources are underlined. The *de novo* synthesis mechanism, which involves formation from carbonaceous sources present in the flyash and particulate matter, generally occurs over hours of residence time as particles remain in the particulate control device. The catalyzed formation mechanism that involves organic precursors catalytically forming dioxins and furans, can occur in-flight as flue gases pass through the optimal temperature window where formation can occur.

Slide 20: De novo synthesis



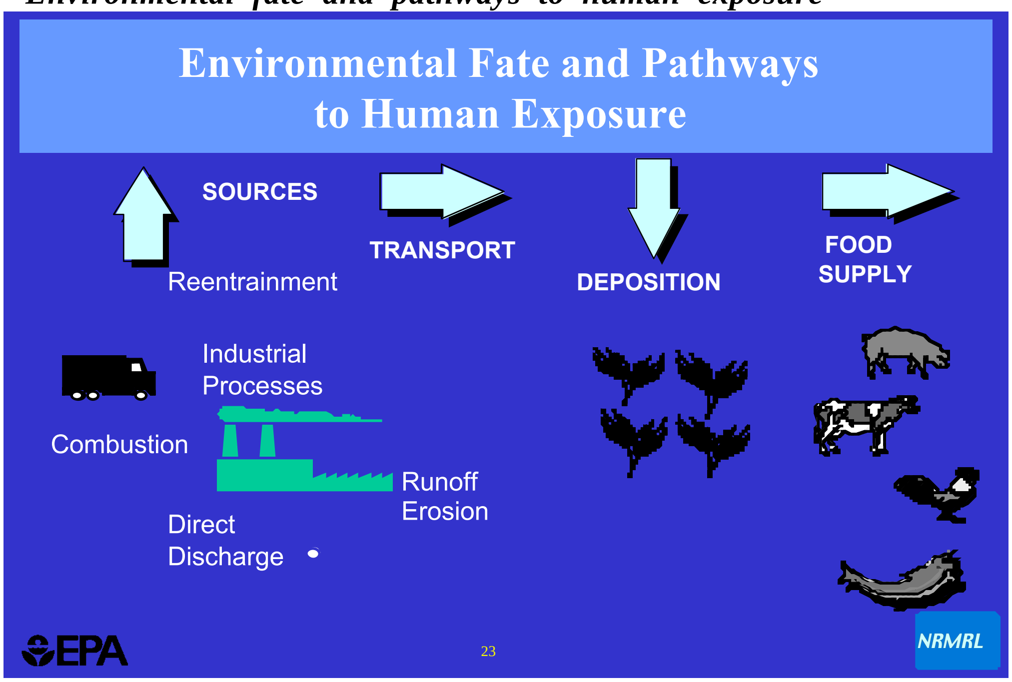
This slide gives additional information on *de novo* synthesis. The photograph is one of an electrostatic precipitator. Note the size of the device relative to the size of the person.

Slide 21: Precursor formation



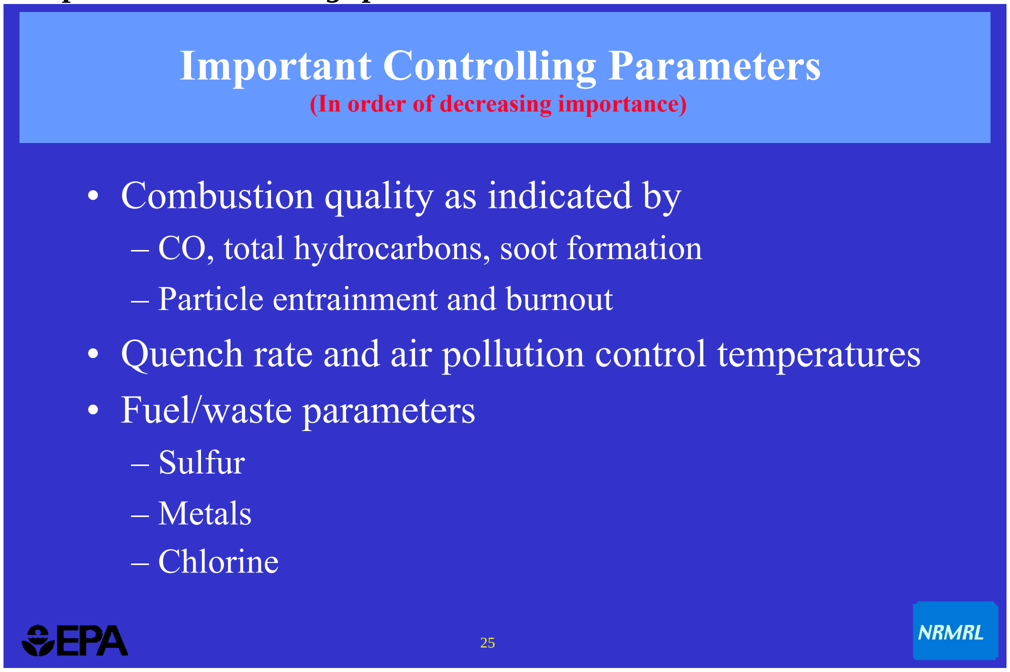
This slide gives additional information on formation through organic precursors. The photograph is that of a stack from a cement kiln burning hazardous waste.

Slide 23: Environmental fate and pathways to human exposure



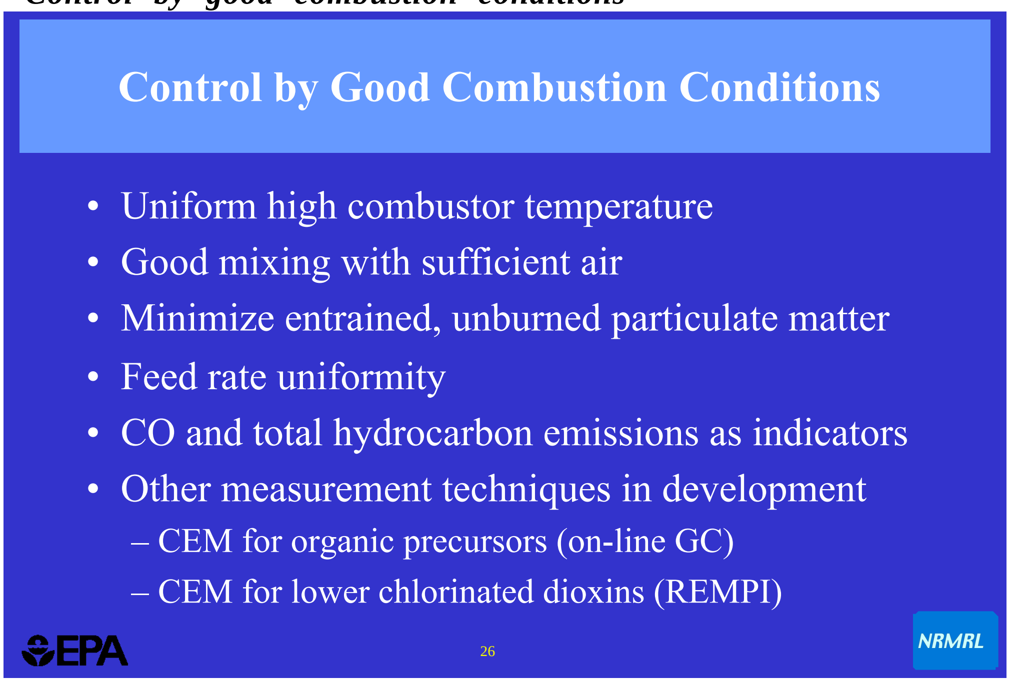
The pathways from dioxin emission source to human consumption are illustrated in this figure. Dioxins emitted from combustion and industrial sources, or re-entrained from environmental reservoirs, are transported to distant locations through atmospheric or aquatic pathways. The dioxins are deposited on agricultural crops, taken up in the food supply, and then bioaccumulated and biomagnified through the food chain. This is the predominant pathway for human exposure, excluding isolated exposure episodes resulting from industrial or waste disposal accidents.

Slide 25: Important controlling parameters



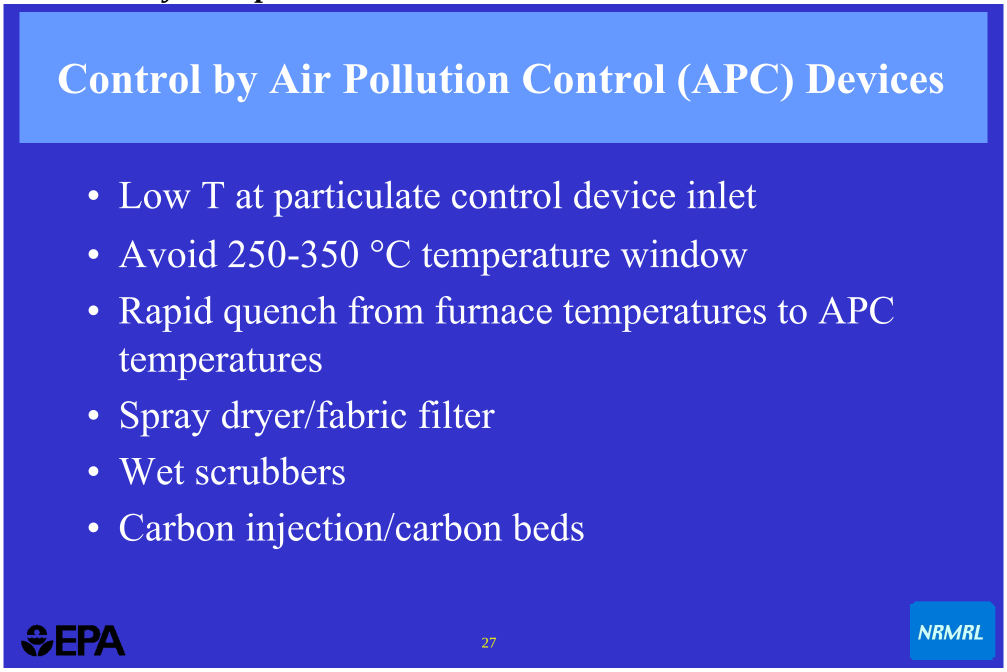
This slide begins the risk management discussion of the presentation. Dioxins from combustion devices can be controlled by simultaneously managing several aspects of the formation process. Assurance of good combustion, coupled with minimization of residence time in the optimal formation temperature window, is the most effective way to reduce dioxin formation. Other risk management aspects, such as fuel/waste parameters, are discussed as well.

Slide 26: Control by good combustion conditions



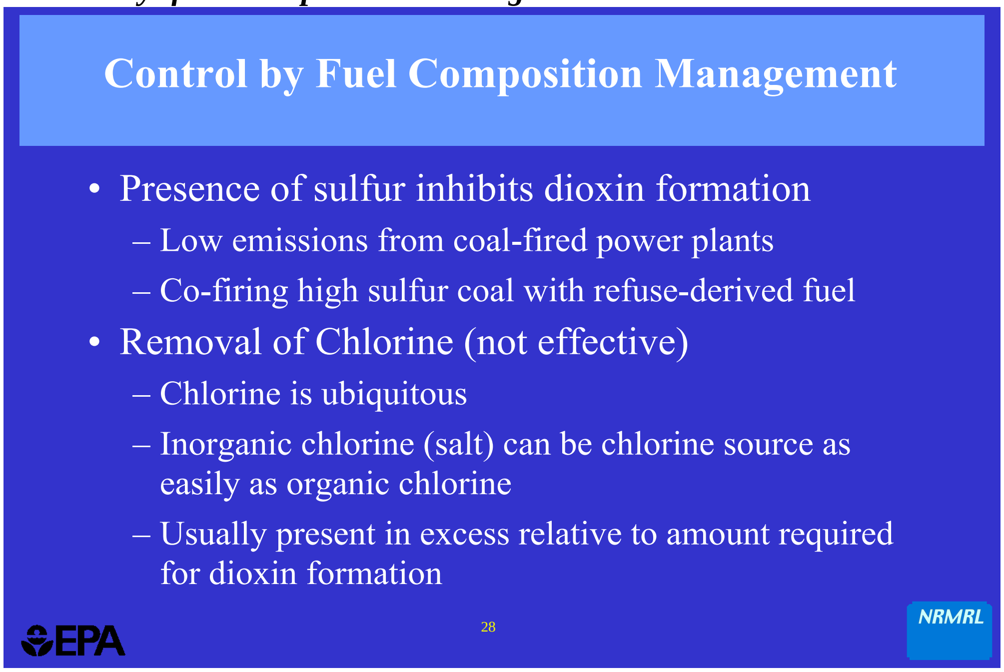
More detail is given on how to ensure good combustion practices to minimize dioxin formation. Some discussion is also given to newly developing methodologies to more directly measure dioxins and dioxin precursors without having to resort to the manual methods in use today.

Slide 27: Control by air pollution control devices



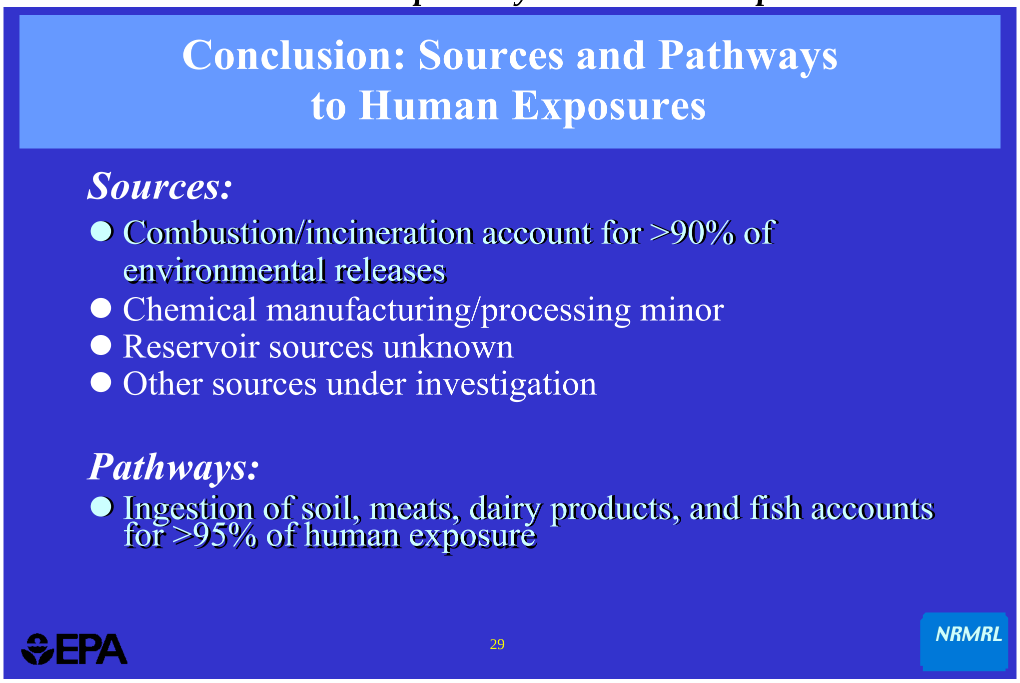
This slide gives more detail on how to operate air pollution control devices to minimize dioxin formation. It also discusses several alternatives for pollution control devices that help to reduce emissions.

Slide 28: Control by fuel composition management



This slide discusses the effect that fuel composition can have on emissions of dioxins. Of particular interest is the potential for reduction of dioxin emissions by addition of sulfur, possibly by firing a high sulfur coal along with chlorinated materials. There is also some discussion of the effectiveness of removal of chlorine from the feed stream. Obviously, if there were no chlorine present, then there could be no emissions of dioxins and furans. However, other parameters that are more controllable have a much greater impact on emissions of dioxins. Effectiveness of combustion, amount of particulate matter carryover, and temperature of the flue gas cleaning device have such a huge impact on emissions of dioxins, that it is not possible to statistically separate out the influence of chlorine input on the emissions from full-scale facilities. Laboratory-scale data show that there is a dependency on chlorine input when all other parameters are held constant; however, it is not possible to perform those types of parametric studies in the field. In addition, there is strong evidence to suggest that the form of the chlorine, whether organic or inorganic, doesn't have a great impact on emissions of dioxins.

Slide 29: Conclusion: sources and pathways to human exposures

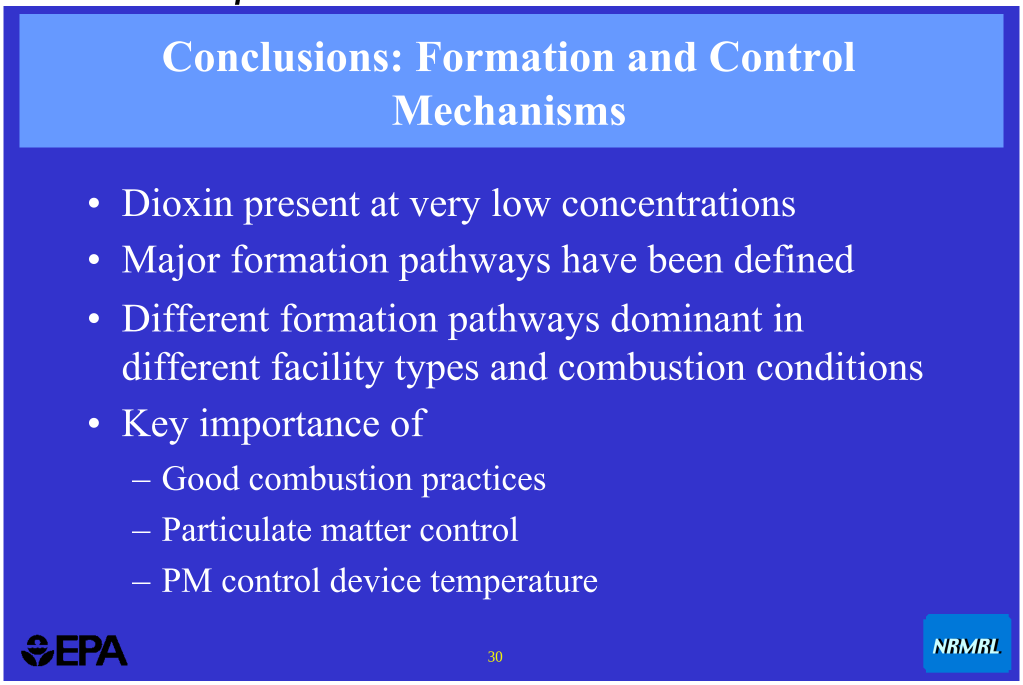


Combustion and incineration sources account for more than 90% of known environmental dioxin releases in the United States. Other sources of exposure, such as chemical manufacture and processing, contribute smaller amounts of dioxin-like substances to the environment. Subsequent human exposure occurs through the food chain, where the ingestion of soil, meats, dairy products, and fish accounts for more than 95% of dioxin intake.

It is important to note that the United States dioxin emission inventory is a work in progress. The contribution to the emission inventory from reservoir sources of dioxin, such as pentachlorophenol-treated utility poles, and other industrial practices, such as metals sintering, remain to be determined. Recent U.S. studies have also indicated that the open burning of household waste in barrels may produce substantial dioxin/furan emissions per kilogram of waste burned. This finding has considerable relevance to developing countries, where the open burning of municipal and other wastes is more widespread.

The 1987 and 1995 inventories support sediment core findings that dioxin emissions in the United States have been declining over recent years. The inventory findings suggest that the replacement of older technologies, equipment, and practices with less polluting alternatives has contributed to this reduction. Data generated throughout this period provide a valuable record of the dioxin emissions resulting from various types and standards of industrial and incineration facilities. Many of these dioxin emission factors will be of relevance to current activities in developing countries. We anticipate that data from this record will be of assistance to other countries should they decide to proceed with national dioxin inventories.

Slide 30: Conclusions: formation and control mechanisms



Dioxin is found in combustor stacks at exceedingly low levels. This leads to very high sampling and analytical costs. New methodologies under development may allow direct continuous measurement of the dioxin precursors or the dioxins themselves. These future developments will allow a much greater degree of process optimization and compliance assurance.

The major dioxin formation mechanisms of dioxin have been defined. Different mechanisms dominate for different sources and different technologies within a source category.

The importance of good combustion practices is reiterated as a practical means of controlling emissions of dioxins.