

Risk & Remediation

Overview of Dioxin Issues

The interest in dioxins as a class of compounds is as persistent as the compounds themselves.

Whether it's based on memories of the evacuation of Times Beach, Missouri in 1982, or through anecdotal familiarity with their presence as contaminants in the Vietnam-era defoliant Agent Orange, nearly everyone recognizes the word "dioxins." But what are dioxins, and where do they come from?

Dioxins comprise a set of structurally-related multi-ring compounds, only some members (congeners) of which exhibit toxicity, chiefly depending on the number and location of chlorine atoms. Those with the highest toxicity are the congeners with four chlorine atoms forming a plane in the 2, 3, 7, 8 positions. The toxicity of each congener is typically expressed as "toxicity equivalents" (TEQs) relative to the most potent of the lot – 2, 3, 7, 8 tetrachlorodibenzo-p-dioxin (TCDD). Note that

the calculation of TEQs can also include certain polychlorinated dibenzofurans (PCDFs) and polychlorinated biphenyls (PCBs) (see Figure 1).

Polychlorinated dibenzo-p-dioxins (PCDDs) and PCDFs are not

synthesized intentionally, but they may be formed during: both naturally-occurring and anthropogenic combustion of organic matter, metal smelting and refining, manufacturing and processing of certain chemicals, biotransformation of biological sources, and photochemical processes. The best-studied source of dioxin generation is combustion of organic material in the presence of chlorine, as may occur in: waste incineration, power generation, uncontrolled combustion such as forest fires and backyard burning, and operation of other high-temperature sources such as cement kilns.

While the factors affecting real-world dioxin generation are not totally understood, the EPA describes three primary mechanisms for generation and release of PCDDs/PCDFs during combustion: (1) release of unaltered PCDDs/PCDFs that

...much of the current environmental load [of dioxins] is the result of the persistence of past releases.

continued on pg. 2

I N S I D E

Overview of Dioxin Issues	1	New Developments in Dioxin Toxicity	4
Letter to our Readers	1	What's New at Gradient	5
Dioxin Sampling: When, Where, and How	3	Guest Editorial: Food Safety – The Industry's Top Priority	6
By The Way	4		

Letter to our Readers

January 2001

Dear Colleague,

In this issue of *Trends*, we focus on dioxins, contentious pollutants that have been a focus of scientific and regulatory interest for decades. We review the chemistry of dioxin and dioxin-like compounds, summarize their sources to the environment, and consider the U.S. EPA's most recent reevaluation of dioxin toxicity. Additionally, we examine the physical and chemical conditions under which dioxins are likely to form, as a guide to making sampling decisions.

Contributors to this issue include Dr. Barbara Beck, Gradient Principal and nationally recognized expert in toxicology and health risk assessment. Joining her are Dr. Eric Butler, a Gradient chemist specializing in development of sampling strategies and forensic techniques, and Dr. Lorenz Rhomberg, a Gradient scientist who served as a member of the EPA's panel for its peer review workshop on dioxin toxicity reassessment. Finally, we welcome Dr. Rhona Applebaum, Executive Vice President of Scientific and Regulatory Affairs for the National Food Processors Association, who shares her thoughts on chemical contamination and food safety issues.

We hope this *Trends* issue provides you with useful insights into the chemistry and toxicity of dioxins, and the implications of their place in our everyday environment.

Yours truly,



Neil Shifrin
President

Trends in Risk & Remediation is a publication of Gradient Corporation. As a national leader in risk assessment and negotiation of risk-based remediation, Gradient offers this publication free of charge to interested groups and individuals. If you have a colleague who would benefit from this publication – or if you have comments or suggestions – please contact Ellen M. Whitman at (617) 395-5000 or email us at trends@gradientcorp.com.



Gradient
CORPORATION

Overview of Dioxin Issues

continued from pg. 1

are present as contaminants in the feed material, (2) formation from thermal breakdown and molecular rearrangement of precursor chlorinated aromatic compounds such as chlorophenols, and (3) *de novo* formation from reactions of fly ash constituents with a metal catalyst. Several factors, such as chlorine and oxygen levels and the temperature of the combustion gases, are particularly important determinants of dioxin formation (U.S. EPA, 2000) (see related article).

Although some PCDDs/PCDFs in the environment come from contemporary sources, such sources are now tightly controlled, and much of the current environmental load is the result of the persistence of past releases. Indeed, owing to widespread environmental redistribution, contemporary local levels, in some cases, may have more to do with nationwide past releases than with current local activities.

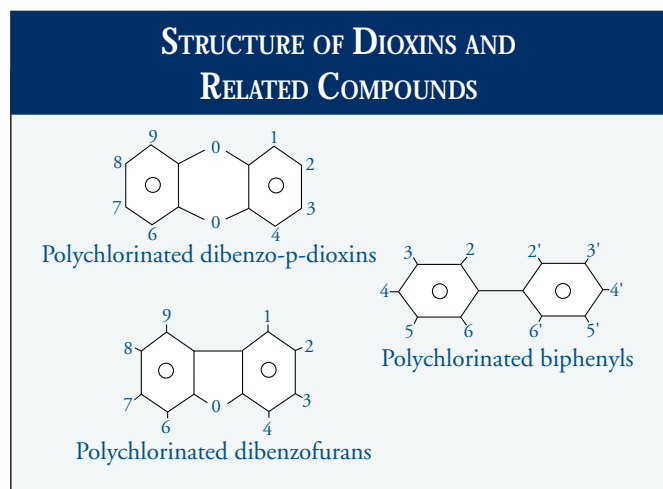


Figure 1.

The relative significance of different environmental sources is an area of continuing discussion and debate. Figure 2 shows current estimates of releases of both anthropogenic and natural PCDDs/PCDFs (expressed as TEQs) to air, water, and land (U.S. EPA, 2000). Waste incineration (mostly municipal waste) appears to be the predominant contemporary source category. However, these results must be interpreted with caution, as indicated by several recent studies. For example, Lemieux and

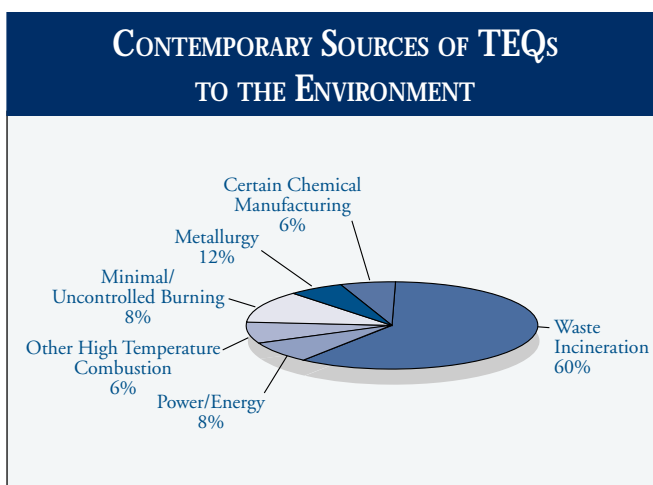


Figure 2. Adapted from the U.S. EPA, 2000.

co-workers (2000) determined that backyard-barrel burning may represent a significant source of ongoing PCDD/PCDF production. And, in fact, the total PCDD/PCDF mass of emissions from a full-scale municipal waste combustor was estimated to be equivalent to backyard burning from only 2.5 to 37 households.

On a final note, it must be recognized that the relative magnitude of different sources of PCDDs/PCDFs to the environment does not necessarily correlate with their importance with respect to human health risk. The risks associated with dioxins are a function of the potential for individuals to be exposed, irrespective of the dioxin's source. Any risk management decisions must consider the current background levels of PCDDs/PCDFs, and the fact that regulation of current emission sources may have little impact on exposure.

Barbara D. Beck, Ph.D.
Email: bbeck@gradientcorp.com

References:

- Lemieux, P.M., C.C. Lutes, J.A. Abbott, and K.M. Aldous. 2000. Emissions of polychlorinated dibenzo-p-dioxins and dibenzofurans from the open burning of household waste in barrels. *Environ. Sci. Technol.* 34:377-384.
- U.S. EPA. 2000. Exposure and Human Health Reassessment of 2, 3, 7, 8 – Tetrachlorodibenzo-p-Dioxin (TCDD) and Related Compounds. Part I: Estimating Exposure to Dioxin-like Compounds. EPA/600/P-00/001A1.

Dioxin Sampling: When, Where, and How

An understanding of dioxin formation can help to inform decisions on sampling strategies.

As with a few other persistent organic pollutants, such as polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), and highly chlorinated pesticides (*e.g.*, DDT), polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) are ubiquitous environmental contaminants. These groups of compounds have experienced atmospheric transport to all areas of the globe. If you look carefully enough, you will find these compounds right outside

... we now have sufficient grasp of the production mechanisms of PCDDs/PCDFs to be able to sensibly decide when sampling and analysis for PCDDs/PCDFs may be necessary.

your office door or in the residential areas near your facility. Does that fact mean you ought to evaluate PCDDs/PCDFs as a matter of course? Probably not. Sampling and analysis for PCDDs/PCDFs can be costly, and in many cases may raise needless anxieties.

When is it prudent to sample for PCDDs/PCDFs? The answer lies in an understanding of their formation. While there is still some uncertainty in the world of PCDD/PCDF formation (see related article), we now have sufficient grasp of the production mechanisms of PCDDs/PCDFs to be able to sensibly decide when sampling and analysis for PCDDs/PCDFs may be necessary.

PCDDs/PCDFs are frequently associated with combustion, and the likelihood of their formation is related to the composi-

tion of the feed material and the operating conditions of the combustor. If there are PCDDs/PCDFs in the feed to an incinerator, the incinerator effluent may contain residual PCDDs/PCDFs that were not destroyed during combustion. If an incinerator has such a feed, then sampling for PCDDs/PCDFs during site investigation is usually warranted.

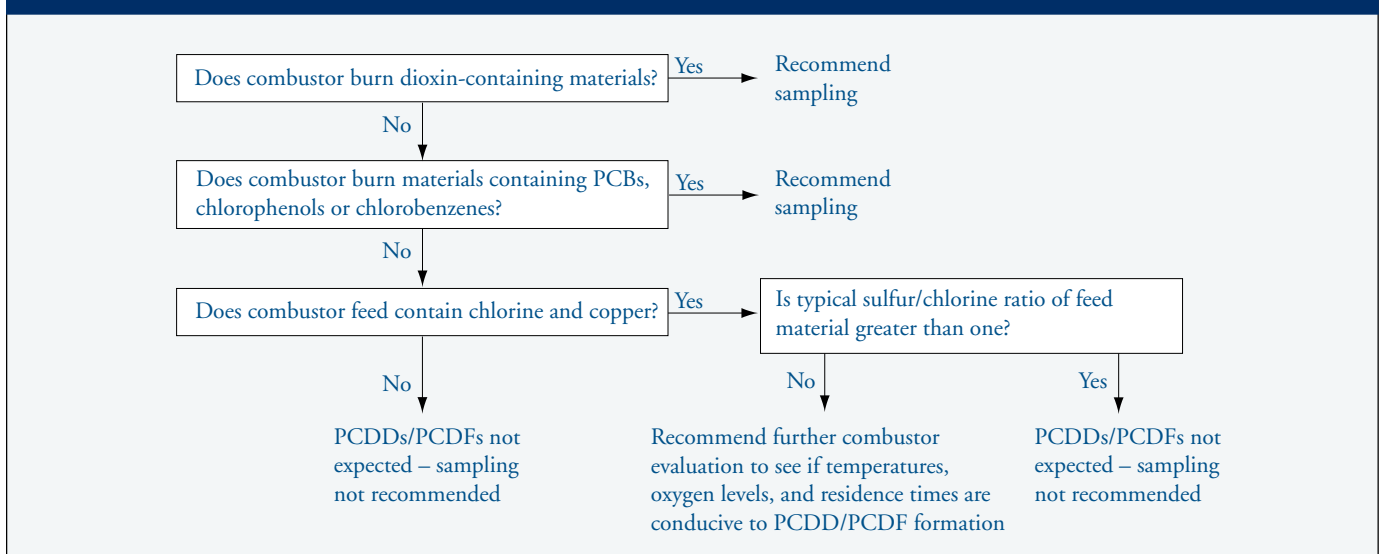
PCDDs/PCDFs are formed during post-furnace interactions (with maximum production of PCDDs/PCDFs at around 250-400°C) between chlorine-containing precursor compounds and organic carbon, usually with a catalyst involved. If the feed contains PCBs, chlorophenols, or chlorobenzenes, then sampling for PCDDs/PCDFs is warranted because, under certain conditions, PCDDs/PCDFs can be formed by the rearrangement of those molecules in the post-furnace environment. For most other feed scenarios, however, one should evaluate the incinerator feed more closely to determine whether or not PCDDs/PCDFs sampling really is necessary.

The formation of PCDDs/PCDFs is partly dependent on the operating conditions of the combustor – temperature, carbon monoxide concentration, residence time of gases at 250-400°C, and the nature of the heat transfer surfaces. PCDD/PCDF formation is also a function of the amount of uncontrolled particulate matter, and, especially, the presence of copper and the relative amounts of chlorine and sulfur.

Reactive chlorine is needed for PCDDs/PCDFs to be formed. If the incinerator feed contains no, or very little, chlorine, then there is little need to sample for PCDDs/PCDFs. If chlorine is present, reactive chlorine may form *via* the Deacon reaction in the oxygen-depleted, post-combustion zone,

continued on pg. 5

DECISION LOGIC FOR DIOXIN/FURAN SAMPLING



New Developments in Dioxin Toxicity

The current fervor over dioxin toxicity sits squarely at the crossroads of science and policy development.

The compounds collectively called “dioxins” arise as unintended byproducts of combustion and certain manufacturing processes. Because these compounds degrade slowly and can gradually accumulate in plant and animal tissues, the small environmental releases over the past decades have led to small but detectable and persistent concentrations in the body tissues of virtually all of us. New releases of dioxins are now tightly controlled, so these “body burdens” are dropping with time, but there has been controversy as to whether current burdens might

...it is important to bear in mind several large uncertainties (some acknowledged by the EPA) in the underlying data and analyses.

have adverse effects on human health.

The U.S. EPA’s reassessment of dioxin toxicity has recently spotlighted the agency’s concerns in this regard, implying cancer risks in the general population

on the order of one in 1000. Many of these conclusions remain controversial, however, and it is important to bear in mind several large uncertainties (some acknowledged by the EPA) in the underlying data and analyses.

The EPA reassessment now classifies tetrachlorodibenzo-p-dioxin (TCDD) as a “human carcinogen” (dropping the earlier qualification of “probable”) even though the epidemiologic data alone remain characterized as “limited” evidence of a causal relationship of TCDD with human cancer. The EPA argues that similarities among humans and animals in the biochemical actions of dioxins justify the firmer conclusion, but many scientists question both the principle of this argument and the biological soundness of its application to dioxins.

The EPA now bases its estimates of dioxin cancer potency on apparent elevations of cancers combined across anatomical sites in human epidemiologic studies. The new cancer slope factor is 10-fold higher than the agency’s 1995 estimate based on liver cancer in rats. The EPA maintains that its reanalysis of the rat data supports this change, but the calculations rely on an unvalidated method for extrapolating animal results to humans that increases the human potency estimate 28-fold over the methods prescribed in the EPA’s risk assessment guidelines. The

use of combined data on all cancers, when most individual kinds of cancer show no significant elevation, is controversial. Moreover, these calculations depend on uncertain estimates of dioxin exposures to industrial workers that occurred decades before the studies commenced. Back-calculation of former body burdens from recently measured blood levels depends on poorly substantiated assumptions about the half-life of dioxin in the body. Critics suggest that the EPA’s half-life estimate is too long, leading to underestimated historic body burdens and, hence, overestimated dioxin potency based on studies of exposed workers.

Finally, only 10% of the background body burden consists of TCDD itself, the balance being a mixture of the various dioxin-like compounds that are measured as TCDD “equivalents” based on order-of-magnitude judgments of relative toxicity. Such rough equivalency assumptions introduce considerable uncertainty, and evidence showing that such mixtures may have effects less than the sum of their components has not been addressed.

These and other uncertainties make conclusions about risks from current body burdens highly questionable. In spite of these uncertainties, a special subcommittee of the EPA’s Science Advisory Board recently approved the dioxin reassessment. Based on this conclusion, it is likely that the EPA will classify dioxins as a human carcinogen, resulting in policy shifts in a number of programs.

Lorenz R. Rhomberg, Ph.D.
Email: lrhomber@gradientcorp.com

BY THE WAY...

New childhood soil ingestion estimates recently published by Stanek and Calabrese suggest that the 95th percentile long-term average rate is approximately 125 mg/day.

Source: Stanek, E.J. and E.J. Calabrese. 2000. Daily soil ingestion estimates for children at a Superfund site. *Risk Analysis* 20:627-636.

What's New at Gradient

Dallas Wait Appointed Editor

Gradient Principal **Dr. A. Dallas Wait** was appointed Associate Editor for the journal *Environmental Forensics*.

Lorenz Rhomberg Appointed to Adjunct Professorship

Dr. Lorenz Rhomberg was recently appointed Adjunct Assistant Professor of Risk Analysis and Environmental Health with the Department of Health Policy and Management at the Harvard School of Public Health.

Recent and Upcoming Presentations

San Antonio, TX. October 19, 2000. Rosalind Schoof. "Consideration of Bioavailability in Deriving Soil Cleanup Levels," presentation at the Fall 2000 Conference of the Interstate Technology Regulatory Cooperation (ITRC). Presentation can be viewed at www.itrcweb.org.

Boston, MA. January 11, 2001. Barbara Beck. "Regulatory Toxicology and Risk Assessment," course lecture on Principles of Toxicology at the Harvard School of Public Health.

Montego Bay, Jamaica. January 22, 2001. Lorenz Rhomberg. "Dose-Response in Non-Cancer Risk Assessment," presentation at the ILSI 2001 Conference.

San Francisco, CA. March 25-29, 2001. Barbara Beck. Co-chair for "Risk Assessment for Metals," course at the 2001 Society of Toxicology Meeting.

San Francisco, CA. March 25-29, 2001. Rosalind Schoof. "Metals Bioavailability," presentation at the 2001 Society of Toxicology Meeting.

San Francisco, CA. March 25-29, 2001. Barbara Beck. "Physiologically-Based Pharmacokinetic Models for Metals," presentation at the 2001 Society of Toxicology Meeting.

San Francisco, CA. March 25-29, 2001. Mara Seeley, Richard Blanchet, Teresa Bowers, et al. "Assessing Public Health Impact from Insecticides Used for Controlling Mosquito-Borne West Nile Virus," poster presentation at the 2001 Society of Toxicology Meeting.

San Francisco, CA. March 25-29, 2001. Tracey Slayton and Barbara Beck. "Mechanistic Differences Between Low Dose and High Dose Effects of Arsenic," poster presentation at the 2001 Society of Toxicology Meeting.

San Francisco, CA. March 25-29, 2001. Tracey Slayton, Barbara Beck, and Tina Souza. "Human Health Risk Assessment for a PCB-Contaminated River," poster presentation at the 2001 Society of Toxicology Meeting.

Trends by Email: If you would prefer to receive *Trends* by email rather than by mail, please let us know by sending us an email at trends@gradientcorp.com.

To request copies of articles or presentations, please contact us at trends@gradientcorp.com or telephone Ellen M. Whitman at (617) 395-5000.

Dioxin Sampling: When, Where, and How

continued from pg. 3

especially in the presence of copper. It is now known, through extensive bench-scale and pilot-scale studies of combustion using a variety of feed materials (municipal waste, coal, and natural gas), that the presence of sulfur inhibits the production of PCDDs/PCDFs, even when other conditions favor their production. The sulfur inhibits PCDD/PCDF formation in at least two ways. The sulfur preferentially reacts with any reactive chlorine that has formed and the sulfur (in the form of sulfur dioxide) reacts with the copper catalyst and deactivates it. It may also be that sulfur can affect PCDD/PCDF formation by sulfonating the phenolic precursors, preventing

subsequent chlorination and biaryl synthesis, or by forming the sulfur analogs of PCDDs/PCDFs.

The bottom line is simply this, if the combustor feed contains chlorine, it is advisable to determine how much sulfur the feed contains. If the molar ratio (sulfur to chlorine) is one or greater, chlorine will not be available to form PCDDs/PCDFs, and sampling for PCDDs/PCDFs may not be necessary (see figure).

Because of the cost of analysis and the stigma associated with dioxins, careful thought must precede any decision to sample for these compounds. Consideration of the need for PCDD/PCDF analysis based on an understanding of the combustor operations and feed materials should precede any development of a sampling plan for PCDDs/PCDFs.

Eric L. Butler, Ph.D.

Email: ebutler@gradientcorp.com

Guest Editorial: Food Safety – The Industry’s Top Priority

Recent discussion of dioxins in the food supply must not divert our attention away from real food safety issues.

It is something of a cliché – but also completely correct – that food safety is the food industry’s top priority. As a result, U.S. consumers enjoy one of the safest food supplies in the world.

There is strong agreement by both the food industry and U.S. government agencies that oversee our food safety system that the nation’s food policies must be based on sound science. Basing food policies on sound science helps to focus food safety efforts on real risks. The chief risks today are food borne pathogens, such as *E. coli O157:H7* and *Salmonella*, which can cause serious illness or death. Food safety activities, including prevention efforts and consumer education, must be targeted at real risks, not speculative ones.

We must not divert valuable resources from true food safety programs to other so-called “food safety” programs that are likely to have little or no impact on the safety of the food supply.

Many “chemical risks” discussed today are much more speculative than real. While there is much scientific disagreement over the threat posed to the food supply by certain chemicals, there can be no disagreement whatsoever that

food borne pathogens pose a true risk. Certainly, the science surrounding food safety continues to evolve, and our knowledge of the impact of various substances, such as dioxin, continues to grow. Dioxin – and the emerging, related topic of “endocrine disruption” – are issues of interest for the food industry. But in terms of our nation’s food safety efforts and policies, we cannot allow our focus to shift away from known dangers. And the fact is that there is much scientific disagreement over the threat

posed to the food supply by certain chemicals, while there is no disagreement whatsoever that food borne pathogens pose a true risk if not addressed properly.

Food safety resources are limited so they must be allocated wisely. We must not divert valuable resources from true food safety programs to other so-called “food safety” programs that are likely to have little or no impact on the safety of the food supply. Shifting spending priorities so that scientifically unsubstantiated risks are given a bigger share of the “resource” pie makes no sense. Dollars and time must be targeted to ensuring progress is made in managing successfully, if not eliminating outright, those risks that are of highest concern. To do otherwise is both irresponsible and dangerous for consumers.

But with all the views and beliefs out there, not to mention the well worn use of the term “precaution,” how best can the public be protected from real vs. perceived risks? The short answer is to use sound, science-based risk assessments to identify the most serious health risks to consumers, and then concentrate on these risks first. Using sound science to focus our resources on real risks is in everyone’s best food safety interest. We in the food industry practice and preach this approach everyday – it’s our top priority!

Rhona S. Applebaum, Ph.D.
Executive Vice President of Scientific and Regulatory Affairs, National Food Processors Association

NFPA is the voice of the \$460 billion food processing industry on scientific and public policy issues involving food safety, nutrition, technical and regulatory matters, and consumer affairs. NFPA’s three scientific centers, its scientists, and professional staff represent food industry interests on government and regulatory affairs and provide research, technical services, education, communications, and crisis management support for the association’s U.S. and international members.

In the next issue:

International Risk Policy Issues

Carcinogen Classification

The Precautionary Principle

Guest Editorial: The U.S. EPA’s Role in International Risk Management

Look for *Trends* on the Web at: www.gradientcorp.com

Copyright © Gradient Corporation 2001.

Photocopying for personal use is permitted.

TRENDS • I N Risk & Remediation

Produced by:

Gradient Corporation

238 Main Street

Cambridge, Massachusetts 02142

Phone: (617) 395-5000

Fax: (617) 395-5001

internet: trends@gradientcorp.com

Printed on recycled paper with soy inks 