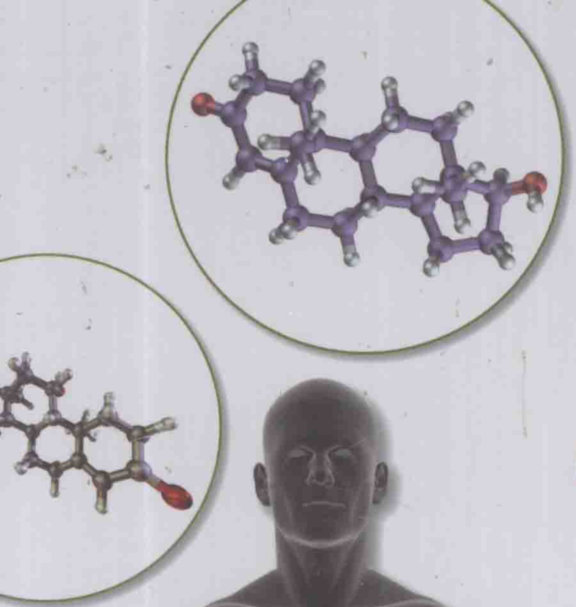
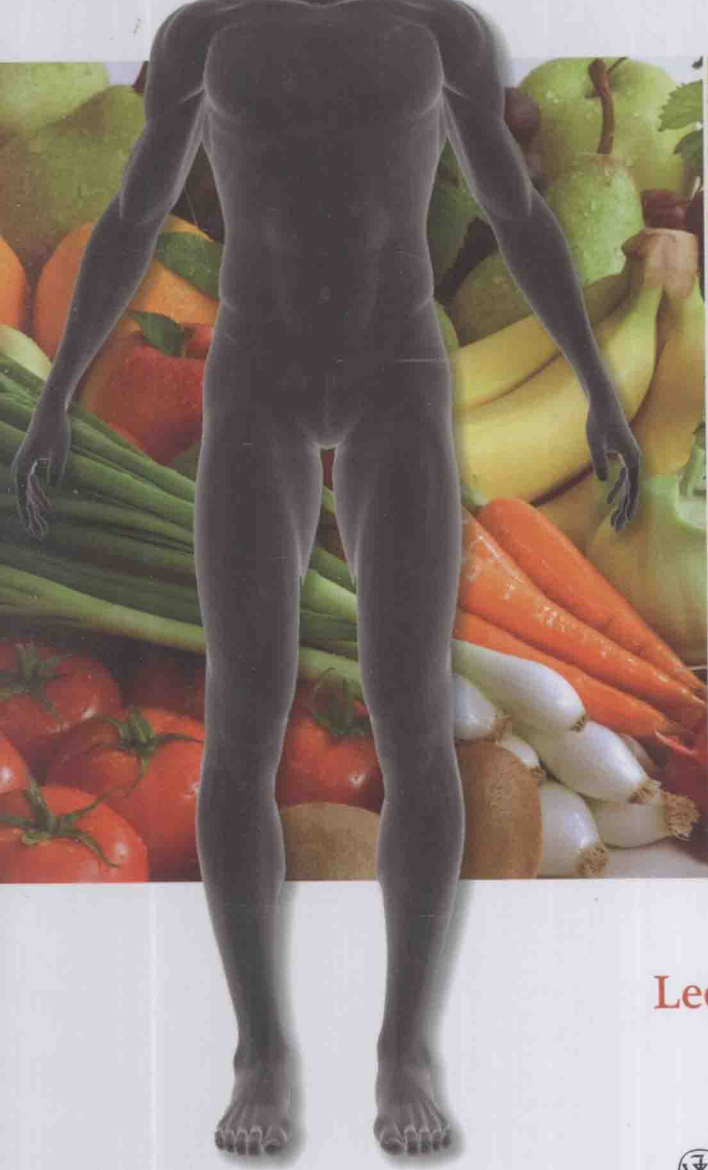


Analysis of Endocrine Disrupting Compounds in Food



Leo M. L. Nollet EDITOR

WILEY-BLACKWELL

Analysis of Endocrine Disrupting Compounds in Food

Leo M.L. Nollet

EDITOR

WILEY-BLACKWELL
A John Wiley & Sons, Inc., Publication

Edition first published 2011

Blackwell Publishing was acquired by John Wiley & Sons in February 2007. Blackwell's publishing program has been merged with Wiley's global Scientific, Technical, and Medical business to form Wiley-Blackwell.

Editorial Office
2121 State Avenue, Ames, Iowa 50014-8300, USA

For details of our global editorial offices, for customer services, and for information about how to apply for permission to reuse the copyright material in this book, please see our Website at www.wiley.com/wiley-blackwell.

Library of Congress Cataloging-in-Publication Data

Analysis of endocrine disrupting compounds in food / editor, Leo M.L. Nollet.
p. cm.
Includes bibliographical references and index.
ISBN 978-0-8138-1816-0 (hardback : alk. paper) 1. Food–Analysis. 2. Endocrine disrupting chemicals–Analysis. I. Nollet, Leo M. L., 1948–
TX541.A75 2011
664'.07–dc22

2010016639

A catalog record for this book is available from the U.S. Library of Congress.

Set in 10 on 12 pt Times by Toppan Best-set Premedia Limited
Printed and bound in Singapore by Fabulous Printers Pte Ltd

1 2011

Analysis of Endocrine Disrupting Compounds in Food

Preface

Many chemical compounds used in the past, and others still used, may have hormone-disrupting properties. Such chemical compounds may interfere with the normal action of hormones in humans and animals. A great number of these endocrine-disrupting compounds are persistent organic pollutants (POPs). POPs may be found worldwide and in every compartment of the environment: water, air, and soil. Animals and humans may inhale or ingest residues of these chemical compounds. Other sources of endocrine disruptors are accidents and pollution.

Analysis of Endocrine Disrupting Compounds in Food provides, first and above all, a unique and comprehensive professional reference source covering most of the recent analytical methodology used to study endocrine-disrupting compounds in food. A broad team of international authors addresses the most recent advances in analysis of endocrine-disrupting chemicals in food. The book further discusses the relationship between chemical compounds and hormone activity. What are the health impacts of different chemical compounds for humans and animals? How are these compounds entering into foodstuffs?

While covering conventional (typically lab-based) methods of analysis, the book focuses on leading-edge technologies that have recently been introduced. The book looks at areas such as food quality assurance and safety. The topics of the presence of persistent organic pollutants; monitoring pesticide and herbicide residues in food; determining heavy and other metals in food; discussing the impact of dioxins, PCBs, PCDFs, and many other suspected chemicals are covered. The book highlights the relevance and importance of sample preparation and cleanup.

Applications of gas chromatography, high-pressure liquid chromatography, and related techniques, and the use of biosensors for evaluating the safety and quality of food and agricultural products are discussed. The reader will also find information on the principles and applications of immunodiagnostics and applications in food safety.

A unique feature of the book is that the informational tables are structured the same way throughout the book; furthermore, most chapters are also structured similarly.

For all their great efforts and their excellent work I thank all of the authors who contributed to this work. It is their efforts that give value to this book.

A special thanks is directed to Mark Barrett and Susan Engelken of Wiley-Blackwell for their support.

I dedicate this book to my fourth grandchild and first grandson, Naut. I hope he will become a respected and loved man in a green world, a world without endocrine disrupting compounds.

Leo M.L. Nollet

Exert your talents, and distinguish yourself, and don't think of retiring from the world, until the world will be sorry that you retire. (Samuel Johnson)

List of Contributors

A. Agüera
Pesticide Residue Research Group
University of Almería
04120 Almería, Spain

Jean-Denis Bailly
Mycotoxicology Research Unit
National Veterinary School of Toulouse
23 Chemin des Capelles
BP 87614
31076 Toulouse Cedex 03, France

Ana Ballesteros-Gómez
Department of Analytical Chemistry
Campus of Rabanales
Edificio Anexo Marie Curie
University of Córdoba
14071 Córdoba, Spain

E. Bizani
Department of Chemistry
Aristotle University of Thessaloniki
54124 Thessaloniki, Greece

Luisa R. Bordajandi
European Food Safety Authority (EFSA)
Unit on Contaminants
Largo N. Palli 5/A. 43100 Parma, Italy

Antonio Canals
Departamento de Química Analítica
Nutrición y Bromatología e Instituto
Universitario de Materiales
Universidad de Alicante
P.O. Box 99
03080 Alicante, Spain

Xu-liang Cao
Food Research Division
Health Canada
251 Sir Frederick Banting Driveway
Tunney's Pasture
Ottawa Ontario K1A 0L2
Canada

Antonia María Carro-Díaz
Dpto. de Química Analítica
Nutrición y Bromatología
Facultad de Química
Instituto de Investigacións e Análises
Alimentarios
Universidad de Santiago de Compostela
Avda. de las Ciencias
s/n 15782 Santiago de Compostela, Spain

Chung-Yu Chen
Department of Chemistry
National Chung Hsing University
Taichung
Taiwan

Ch. Christophoridis
Department of Chemistry
Aristotle University of Thessaloniki
54124 Thessaloniki, Greece

E. Evgenidou
Department of Chemistry
Aristotle University of Thessaloniki
54124 Thessaloniki, Greece

Iván P. Román Falcó
Departamento de Química Analítica
Nutrición y Bromatología e Instituto
Universitario de Materiales
Universidad de Alicante
P.O. Box 99
03080 Alicante
Spain

Yong-lai Feng
Exposure and Biomonitoring Division
Health Canada
50 Columbine Driveway
Tunney's Pasture
Ottawa Ontario K1A 0K9
Canada

A.R. Fernández-Alba
IMDEA (Instituto Madrileño de
Estudios Avanzados)
Parque Científico Tecnológico de la
Universidad de Alcalá
28805 Alcalá de Henares, Madrid
Spain
Pesticide Residue Research Group
University of Almería
04120 Almería, Spain

K. Fytianos
Department of Chemistry
Aristotle University of Thessaloniki
54124 Thessaloniki, Greece

Juan F. García-Reyes
Analytical Chemistry Research Group
Department of Physical and Analytical
Chemistry
University of Jaen
23071 Jaén, Spain

Bienvenida Gilbert-López
Analytical Chemistry Research Group
Department of Physical and Analytical
Chemistry
University of Jaen
23071 Jaén, Spain

Belén Gómara
Instrumental Analysis and Environmental
Chemistry Department
General Organic Chemistry Institute, CSIC
Juan de la Cierva 3, 28006 Madrid
Spain

M.J. Gómez
IMDEA (Instituto Madrileño de Estudios
Avanzados)
Parque Científico Tecnológico de la
Universidad de Alcalá
28805 Alcalá de Henares, Madrid
Spain
Department of Chemical Engineering
University of Alcala
28771 Alcala de Henares, Madrid
Spain

M.M. Gómez-Ramos
Pesticide Residue Research Group
University of Almería
04120 Almería, Spain

María José González
Instrumental Analysis and Environmental
Chemistry Department
General Organic Chemistry Institute, CSIC
Juan de la Cierva 3, 28006 Madrid
Spain

D. Lambropoulou
Department of Chemistry
Aristotle University of Thessaloniki
54124 Thessaloniki, Greece

Maw-Rong Lee
Department of Chemistry
National Chung Hsing University
Taichung
Taiwan

Rosa Antonia Lorenzo-Ferreira
Dpto. de Química Analítica
Nutrición y Bromatología
Facultad de Química
Instituto de Investigacións e Análises Alimentarios
Universidad de Santiago de Compostela
Avda. de las Ciencias
s/n 15782 Santiago de Compostela, Spain

M.A. Martínez-Uroz
Pesticide Residue Research Group
University of Almería
04120 Almería, Spain

Manuela Melis
Laboratory of Food Toxicology
Department of Environmental Health Sciences
Mario Negri Institute for Pharmacological Research
Via La Masa 19, 20156 Milan, Italy

Antonio Molina-Díaz
Analytical Chemistry Research Group
Department of Physical and Analytical Chemistry
University of Jaen
23071 Jaén, Spain

Leo M.L. Nollet
University College Ghent
Member of Ghent University Association
Faculty of Applied Engineering Sciences
Schoonmeersstraat 52
B9000 Gent
Belgium

Soledad Rubio
Department of Analytical Chemistry
Campus of Rabanales
Edificio Anexo Marie Curie
University of Córdoba
14071 Córdoba, Spain

Bing Shao
Institute of Nutrition and Food Hygiene
Beijing Center for Disease Control and Prevention
Beijing 100013, China

Peter Šimko
Food Research Institute
Priemyselna 4
824 75 Bratislava
Slovak Republic
and
Institute of Food Science and Biotechnology
Faculty of Chemistry
Brno University of Technology
Purkyňova 464/118, 612 00 Brno
Czech Republic

Ashok K. Singh
Department of Veterinary Diagnostic Medicine
College of Veterinary Medicine
University of Minnesota, St Paul Campus
1333 Gortner Ave
St Paul, MN 55108
USA

Joseph Sneddon
Department of Chemistry
McNeese State University
Lake Charles, LA 70609
USA

Lorena Vidal
Departamento de Química Analítica
Nutrición y Bromatología e Instituto Universitario de Materiales
Universidad de Alicante
P.O. Box 99
03080 Alicante, Spain

Rong Wang
Exposure and Biomonitoring Division
Health Canada
50 Columbine Driveway
Tunney's Pasture
Ottawa Ontario K1A 0K9
Canada

Guang-Guo Ying
State Key Laboratory of Organic Geochemistry
Guangzhou Institute of Geochemistry
Chinese Academy of Sciences
511 Kehua Street, Tianhe District
Guangzhou 510640, China

Zulin Zhang
The Macaulay Institute
Craigiebuckler
Aberdeen, AB15 8QH, UK

John L. Zhou
School of Life Sciences
Science
University of Sussex
Falmer, Brighton BN1 9QG, UK

Jipin Zhu
Exposure and Biomonitoring Division
Health Canada
50 Columbine Driveway
Tunney's Pasture
Ottawa Ontario K1A 0K9
Canada

Ettore Zuccato
Laboratory of Food Toxicology
Department of Environmental Health Sciences
Mario Negri Institute for Pharmacological Research
Via La Masa 19, 20156 Milan, Italy

Table of Contents

Analysis of Endocrine Disrupting Compounds in Food

Chapter 1

Endocrine Disrupting Chemicals. What? Where?

Guang-Guo Ying

Introduction

There is a concern that some natural and synthetic chemicals can interfere with the normal functioning of endocrine systems, thus affecting reproduction and development in wildlife and humans. These chemicals are called *endocrine disruptors* or *endocrine-disrupting chemicals* (EDCs). Although endocrine disruption has been known since the 1930s (Dodds et al. 1938), this issue has regained attention and generated immense scientific and public interest since 1992 (Colborn and Clement 1992), and especially since the publication of the book *Our Stolen Future* (Colborn et al. 1996). The chemicals identified or suspected as being endocrine disruptors in the literature include pesticides (e.g., dichlorodiphenyltrichloroethane [DDT], dichlorodiphenyldichloroethylene [DDE], dieldrin, endosulfan), pharmaceuticals (e.g., diethylstilbestrol [DES]) and industrial chemicals or pollutants (e.g., polychlorinated biphenyls [PCBs], dioxins, bisphenol A) (Table 1.1). Since then, many studies have been carried out on endocrine disruption. Some reproductive problems in wildlife and humans have been linked to exposure to these chemicals. Wildlife and humans are exposed daily to these pervasive chemicals that have already caused numerous adverse effects in wildlife and are most likely affecting humans as well.

There is compelling evidence regarding the effects of exposure to EDCs on wildlife (Damstra et al. 2002). These include imposex of mollusks by organotin compounds (Alzieu 2000; Gibbs et al. 1990; Horiguchi et al. 1994); developmental abnormalities, demasculinization and feminization of alligators in Florida by organochlorines (Guillette et al. 1994, 2000); and feminization of fish by wastewater effluent from sewage treatment plants and paper mills (Table 1.2) (Jobling et al. 1998; Bortone et al. 1989). There is also evidence that human testicular and breast cancer rates have increased during the last four decades, especially in developed countries (Brown et al. 1986; Hakulinen et al. 1986; Adami et al. 1994; Feuer 1995; Moller 1993; Ries et al. 1991; Wolff et al. 1993). However, except in a few cases (e.g., DES), a causal relation between exposure to chemicals and adverse health effects in humans has not been firmly established. Owing to the scientific evidence and public concern about potential effects on humans and wildlife, the U.S. Congress made amendments to the Safe Drinking Water Act (SDWA) in 1996 and required the U.S. Environmental Protection Agency (U.S. EPA) to develop a screening program for endocrine disruptors (Fenner-Crisp et al. 2000). In April 2000, a meeting of the environment ministers of the G8 group of industrialized countries listed EDCs as one of the high priorities and called for a furtherance of knowledge acquisition

Analysis of Endocrine Disrupting Compounds in Food, edited by Leo M.L. Nollet © 2011 Blackwell Publishing, Ltd

Table 1.1. List of suspected/known EDCs.

Classification	Endocrine-Disrupting Chemicals	
Pesticides	2,4-D	Kepone (chlordecone)
	Atrazine	Lindane
	Benomyl	Malathion
	Carbaryl	Mancozeb
	Chlordane (γ-HCH)	Methomyl
	Cypermethrin	Methoxychlor
	DDT and its metabolites	**Mirex**
	Dicofol	Parathion
	Dieldrin/Aldrin	Pentachlorophenol
	Endosulfan	Permethrin
	Endrin	Simazine
	Heptachlor	Toxaphene
	Hexachlorobenzene (HCB)	Trifluralin
	Iprodione	Vinclozolin
Organohalogens	Dioxins and furans	PBBs and PBDEs
	PCBs	2,4-Dichlorophenol
Alkylphenols	Nonylphenols	Nonylphenol ethoxylates
	Octylphenols	Octylphenol ethoxylates
	Pentaphenols	Butylphenols
Heavy metals	Cadmium	Mercury
	Lead	Arsenic
Organotins	Tributyltin	Triphenyltin (TPhT)
Phthalates	Diethylhexyl phthalate	Dihexyl phthalate
	Butyl benzyl phthalate	Dipropyl phthalate
	Di-*n*-butyl phthalate	Dicyclohexyl phthalate
	Di-*n*-pentyl phthalate	Diethyl phthalate
Natural hormones	17β-Estradiol	Estriol
	Estrone	Testosterone
Pharmaceuticals	Ethinyl estradiol	Tamoxifen
	Mestranol	Diethylstilbestrol (DES)
Phytoestrogens	Isoflavonoids	Zearalenone
	Coumestans	β-sitosterol
	Lignans	
Phenols	Bisphenol A	Bisphenol F
Aromatic hydrocarbons	Benzo(*a*)pyrene	Anthracene
	Benz(*a*)anthracene	Pyrene
	Benzo(*b/h*)fluoranthene	Phenanthrene
	6-hydroxy-chrysene	*n*-Butyl benzene

on EDCs through jointly planned and implemented projects and international information sharing (Loder 2000). Surveys of some new emerging endocrine disrupting chemicals (e.g., nonylphenol and steroids) in major rivers of some countries have been undertaken (e.g., Naylor et al. 1992; Blackburn et al. 1999; Ahel et al. 2000; Tabata et al. 2001; Kolpin et al. 2002). The U.S. EPA and the Organization of Economic and Cooperative Development (OECD) have invested considerable resources to develop tiered procedures for the testing and assessment of EDCs (Fenner-Crisp et al. 2000; Huet 2000; Parrott et al. 2001). The U.S. EPA planned to screen 15,000 chemicals for their possible effects as endocrine disruptors in animals and humans (Macilwain 1998).

This chapter will give some background information about the endocrine disruption

Table 1.2. Effects associated with exposure to EDCs in wildlife (representative examples).

Organism	Chemical(s)	Effect	References
Alligators (Lake Apopka)	DDT and its metabolites (DDD and DDE), dicofol and other pesticides	Demasculinization, reproductive dysfunction	Guillette et al. (1994) Guillette et al. (1995) Guillette et al. (2000) Pickford et al. (2000)
Fish (roach, trout) (Rivers in UK)	Hormone steroids and nonylphenols from STP effluents	Feminization, abnormal gonad and gonoduct development	Purdom et al. (1994) Jobling and Sumpter (1993) Jobling et al. (1998)
Fish (Rivers in Canada and Finland)	Chemicals from pulp and paper mill effluents	Delayed sexual maturity, smaller gonads, reduced fecundity and changed sex steroid levels	Aaltonen et al. (2000) Karels et al. (1999) McMaster et al. (1995) Munkittrick et al. (1997)
Fish (salmon) (Great Lakes)	PCBs, dioxins, and organochlorine pesticides	Abnormal thyroid function	Leatherland (1993)
Birds (gulls, bald eagles) (Great Lakes, and California coast)	PCBs, DDT, and DDE	Feminization, abnormal thyroid function, supernormal clutches, and decreased hatchability	Bowerman et al. (2000) Fry et al. (1987) Moccia et al. (1986)
Invertebrates (snails, mussels, clams, oysters)	Tributyltin (TBT)	Masculinization (imposex)	Alzieu (1998, 2000) Gibbs and Bryan (1986) Gibbs et al. (1988) Jha et al. (2000a) Jha et al. (2000b) Morcillo and Porte (2000)
Sheep	Phytoestrogens	Decreased fertility	Bennetts et al. (1946) Hughes (1988)

issue, EDCs in food, and potential effects associated with exposure to EDCs.

Endocrine-disruption chemicals

Endocrine system

An endocrine system is found in nearly all animals, including mammals, nonmammalian vertebrates (e.g., fish, amphibians, reptiles and birds) and invertebrates (e.g., snails, lobsters, insects, and other species). Along with the nervous system, the endocrine system is one of the two communication systems that regulate all responses and functions of the body. The endocrine system consists of glands and the hormones they produce that guide the development, growth, reproduction, and behavior of humans and animals. The major endocrine glands of the body include the pituitary, thyroid, parathyroids, adrenals, pancreas, pineal gland, and gonads (ovaries in females and testes in males). Hormones are biochemicals that are produced by endocrine glands in one part of the body, travel through the bloodstream, and cause responses in other parts of the body. They act as chemical messengers and interact with specific receptors in cells to trigger responses and prompt normal biological functions such as growth, reproduction, and development.

Hormones generally fall into four main categories: (1) amino acid derivatives, (2) proteins, (3) steroids, and (4) eicosanoids (Lister and van der Kraak 2001). The unifying nature of hormone action is the presence of receptors on target cells, which bind a specific hormone with high affinity and stereospecificity. Steroid and thyroid hormones act by entering target cells and stimulating specific genes. All other hormones bind to receptors on the cell surface and activate second-messenger molecules within the target cells (Raven and Johnson 1999). The body has hundreds of different kinds of receptors; each one is

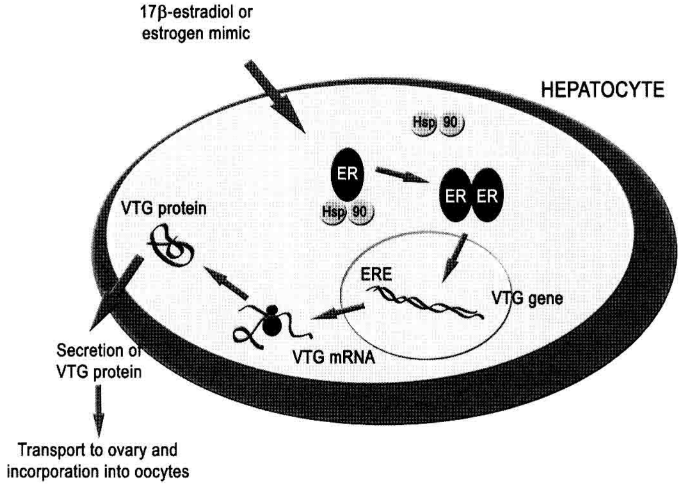


Figure 1.1. Functioning of hormone system. VTG, vitellogenin; ER, estrogen receptor; Hsp90, heat shock protein 90 kDa; ERE, estrogen response element.

designed to receive a particular kind of chemical signal. The hormone and its receptor have a "lock-and-key" relationship (Figure 1.1). When a hormone encounters its receptor, they grab hold, engaging in a molecular embrace known as *binding*. Once joined, the hormone molecule and its receptor trigger the production of particular proteins that turn on the biological activity associated with the hormone. The actions of hormones have two types: organizational and activational (Lister and van der Kraak 2001). The first type of action occurs during critical periods of development and induces permanent effects such as the actions of sex steroids. The second type of action causes only transient changes in a myriad of cellular processes such as the effects of glucagon and insulin on glucose homeostasis. Organizational actions are more important in terms of effect with respect to environmental contaminants (Guillette et al. 1996). Timing of hormone release is often critical for normal function, especially during fetal development (Palanza et al. 1999).

Endocrine disruption

The Society of Environmental Toxicology and Chemistry (SETAC) defined endocrine disruption as follows: "Synthetic, and naturally occurring, chemical substances in the environment are disrupting the normal functions of the endocrine system and its hormones in humans and wildlife" (SETAC 2000). This hypothesis has received much attention in recent years because there is increasing evidence that some chemicals in our environment disrupt the endocrine systems in wildlife as well as humans.

There are several ways that chemicals can interfere with the endocrine system (Sonnenschein and Soto 1998). They can mimic or block natural hormones and alter hormonal levels, thus affect the functions that these hormones control. Less direct disruption involves alteration of the body's ability to produce hormones, interference with the ways hormones travel through the body, and changes in numbers of receptors. Regardless of the situation, having too much or too little of the hormones it needs may cause the endocrine system to function inappropriately. Very subtle disruptions of the endocrine system can result in changes in growth, development, or behavior that can affect the organism itself or the next generation (Guillette et al. 1996; vom Saal et al. 1997; Palanza et al. 1999).