Jerome O. Nriagu
Milagros S. Simmons

Food Contamination from Environmental Sources

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23

FOOD CONTAMINATION FROM ENVIRONMENTAL SOURCES

Edited by

Jerome O. Nriagu

National Water Research Institute
Burlington, Ontario, Canada

and

Milagros S. Simmons

University of Michigan
Ann Arbor, Michigan

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JEROME O. NRIAGU, Series Editor

CONTRIBUTORS

ALBERTS, L. A., Instituto Nacional de Investigaciones Sobre Recursos Bioticos, Xalapa, Ver., Mexico

ASHOKE, M., Department of Environmental and Occupational Health, University of South Florida, Tampa, Florida

AZCUE, J. M., National Water Research Institute, Burlington, Ontario, Canada

CAPPON, C. J., Environmental Health Sciences Center, University of Rochester Medical Center, Rochester, New York

CASALE, W. L., Department of Food Science and Human Nutrition, Michigan State University, East Lansing, Michigan

CONACHER, H. B. S., Health and Welfare Canada, Banting Research Centre, Ottawa, Ontario, Canada

DAVIES, K., Department of Public Health, City Hall, Toronto, Ontario

DE LEON, R., Department of Microbiology and Immunology, University of Arizona, Tucson, Arizona

DHALIWAL, G. S., College of Agriculture, Punjab Agricultural University, Ludhiana, India

ELIAS, R. W., United States Environmental Protection Agency, Research Triangle Park, North Carolina

FLEGAL, A. R., Institute of Marine Sciences, University of California, Santa Cruz, California

FRANK, R., Ontario Ministry of Agriculture and Food, University of Guelph, Guelph, Ontario

GERBA, C. P., Department of Microbiology and Immunology, University of Arizona, Tucson, Arizona

GRIFFITHS, M. W., The Hannah Research Institute, Ayr, Scotland

HARGITAI, F., Department of Plant Protection and Agrochemistry, Ministry of Agriculture and Food, Budapest, Hungary

HEIKES, D. L., Department of Health and Human Services, Food and Drug Administration, Kansas City, Missouri

KHAYAT, A., Scientific and Analytical Services, Beatrice/Hunt–Wesson Inc., Fullerton, California

KULKARNI, A. P., Department of Environmental and Occupational Health, University of South Florida, Tampa, Florida

LAWRENCE, J. F., Bureau of Chemical Safety, Health and Welfare Canada, Banting Research Centre, Ottawa, Ontario

LUPIEN, J. R., Food Quality and Standards Service, FAO – United Nations, Rome, Italy

MATTHEES, D. P., Department of Chemistry, South Dakota State University, Brookings, South Dakota

NRIAGU, J. O., National Water Research Institute, Burlington, Ontario

PAGE, B. D., Health and Welfare Canada, Banting Research Centre, Ottawa, Ontario, Canada

PESTKA, J. J., Department of Food Science and Human Nutrition, Michigan State University, East Lansing, Michigan

PHILLIPS, J. D., The Hannah Research Institute, Ayr, Scotland

RIPLEY, B. D., Ontario Ministry of Agriculture and Food, Guelph, Ontario, Canada

SINGH, B., Department of Entomology, Punjab Agricultural University, Ludhiana, India

SINGH, P. P., Department of Entomology, Punjab Agricultural University, Ludhiana, India

SMART, N. A., Ministry of Agriculture, Fisheries and Food, Harpenden Laboratory, Hatching Green, Harpenden, United Kingdom

SMITH, D. R., Department of Biology, University of California, Santa Cruz, California

STACEY, C. I., School of Applied Chemistry, Curtin University of Technology, Bentley, Western Australia

TODD, E. C. D., Health Protection Branch, Health and Welfare Canada, Ottawa, Ontario

INTRODUCTION TO THE SERIES

The deterioration of environmental quality, which began when mankind first congregated into villages, has existed as a serious problem since the industrial revolution. In the second half of the twentieth century, under the ever increasing impacts of exponentially growing population and of industrializing society, environmental contamination of the air, water, soil, and food has become a threat to the continued existence of many plant and animal communities of various ecosystems and may ultimately threaten the very survival of the human race. Understandably, many scientific, industrial, and governmental communities have recently committed large resources of money and human power to the problems of environmental pollution and pollution abatement by effective control measures.

Advances in Environmental Sciences and Technology deals with creative reviews and critical assessments of all studies pertaining to the quality of the environment and to the technology of its conservation. The volumes published in the series are expected to service several objectives: (1) stimulate interdisciplinary cooperation and understanding among the environmental scientists; (2) provide the scientists with a periodic overview of environmental developments that are of general concern or that are of relevance to their own work or interests; (3) provide the graduate student with a critical assessment of past accomplishment, which may help stimulate him or her toward the career opportunities in this vital area; and (4) provide the research manager and the legislative or administrative official with an assured awareness of newly developing research work on the critical pollutants and with the background information important to their responsibility.

As the skills and techniques of many scientific disciplines are brought to bear on the fundamental and applied aspects of the environmental issues, there is a heightened need to draw together the numerous threads and to present a coherent picture of the various research endeavors. This need and the recent tremendous growth in the field of environmental studies have clearly made some editorial adjustments necessary. Apart from the changes in style and format, each future volume in the series will focus on one particular theme or timely topic,

starting with Volume 12. The author(s) of each pertinent section will be expected to critically review the literature and the most important recent developments in the particular field; to critically evaluate new concepts, methods, and data; and to focus attention on important unresolved or controversial questions and on probable future trends. Monographs embodying the results of unusually extensive and well-rounded investigations will also be published in the series. The net result of the new editorial policy should be more integrative and comprehensive volumes on key environmental issues and pollutants. Indeed, the development of realistic standards of environmental quality for many pollutants often entails such a holistic treatment.

JEROME O. NRIAGU, Series Editor

PREFACE

Every chemical released into the ecosystem has the potential of getting into the human food chain. It is therefore not surprising that our foods now contain a large number of chemical and biological contaminants derived either directly or indirectly from the environment. For the general population, the diet has become the major exposure route for most of the known toxic contaminants in the environment. What we now eat probably represents a good index of the persistent contaminants being discharged into our environment. Although food contamination has been of public health concern for many years, most of the publications on this topic deal with food additives used as preservatives, colorants, and flavoring, or with contamination problems associated with food production, processing, packaging, or storage. Little attention has been paid to the accumulation and transfer of contaminants through the food chain to the human consumer.

This volume, aimed at filling this critical gap in knowledge, deals with the accumulation and persistence of toxic contaminants in the human food chain; it addresses the violation of the long-held belief that "if it's natural, it must be good." It provides critical and timely reviews on the detection, sources, distribution, speciation and bioavailability of environmental contaminants and their metabolites in various food products. The toxicological and health significance of the observed contaminant levels in foods has also been discussed. Thus, the volume covers a subject of great interest in food science and public health. It should also be fundamental reading for anyone concerned about the quality of our foods and how it is being affected by industrial discharges into the environment.

Any success of this volume belongs to our distinguished authors. We thank the staff of John Wiley & Sons, Inc., New York for invaluable editorial assistance.

Burlington, Ontario

Ann Arbor, Michigan

JEROME O. NRIAGU

MILAGROS S. SIMMONS

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AGRICULTURAL AND RELATED CHEMICAL CONTAMINATION IN FOODS: A HISTORICAL PERSPECTIVE

Duane P. Matthees

Department of Chemistry, South Dakota State University, Brookings, South Dakota 57007–1217

1. CONCEPT OF ENVIRONMENTAL CONTAMINANTS IN FOODS

Environmental contaminants in foods are considered to be compounds that are not normal food constituents and that inadvertantly find their way into food products and cannot readily be removed by the usual manufacturing practices. These compounds are sometimes used intentionally, such as pesticides, and, in this case, the amounts remaining in food products are usually referred to as residues (which does not evoke the same negative connotations as the term "contaminant"). Some people would prefer to consider contaminants as any synthetic compound in foods, although others would reserve this term for harmful or illegal amounts of various chemicals. In any case, most would agree that large amounts of residues are considered to be contaminants. Many individuals are uncomfortable with the idea that they are ingesting varying amounts of pesticides and industrial chemicals, and the controversy over residues and the concept of legal tolerances has been a long one.

Many people think of environmental contaminants as extremely durable, persistent, bioaccumulating compounds that are excreted only very slowly. Although some compounds, such as the polychlorinated biphenyls and hexachlorobenzene, fit this description, there are other compounds that are excreted more rapidly, but are still toxic when ingested in small amounts; these compounds can be potential threats to the food supply. Although compounds used today are less persistent than some of the compounds used in the past, their biological activity, although of shorter duration, may be much greater.

2. CHEMICAL ANALYSIS OF FOOD CONTAMINANTS

2.1. Introduction

The history of environmental contamination of foods might to a large extent be termed the history of the *detection* of environmental contaminants, since contamination is otherwise not detected unless illness results. Moreover, unless enough individuals are affected so that an incident is studied from an epidemiological viewpoint, an isolated instance of toxicity may well be overlooked, in the absence of chemical evidence.

The pesticide residue analyst of the early twentieth century needed methods for the analysis of only arsenic and possibly of copper in Bordeaux mixture; the emphasis in food analysis at that time was the detection of adulterants more than the detection of spray residues. Although pesticides were undoubtedly toxic, it was apparently felt that the residues were low anyway and thus possibly of less

concern than the preservatives and adulterants that might be present in fairly large amounts. Moreover, while spraying of crops for insect control was not particularly controversial for many people, adulteration involved dishonesty and possible health effects at the same time. As will be seen later, there was some discussion on the effects of arsenic residues, but the proposed tolerances for arsenic were the issue rather than the use of insecticides per se.

For these and other reasons, food analysis earlier in this century was not unduly preoccupied with trace analysis at all, let alone pesticide residue analysis.

Organic chemical analysis was slow to develop. Until recently, many introductory quantitative analysis textbooks scarcely acknowledged the existence of organic compounds, let alone any need for their analysis. Organic analysis, especially trace analysis, presents some unique problems. There are so many organic compounds, relative to inorganic, that it is more difficult to use a standard sample treatment. In contrast to inorganic analysis, in which organic matter can be decomposed to facilitate the analytical process, organic analysis requires that the compounds be extracted in unaltered form from a variety of sample matrices. Thus, environmental and food samples are difficult to extract quantitatively. In addition, there were a limited number of analytical methods that would identify or quantify organic compounds in a mixture. Barger (1914) noted that chemical methods were of little value in the determination of organic poisons in foods; he preferred physiological methods of detection. Higgins (1914) assayed for food toxins by subcutaneous injection of extracts into guinea pigs. The need for better methods of organic chemical analysis became more obvious in the 1930s and later as the synthetic chemical industry and petrochemical industry grew.

2.2. Colorimetric Methods

The use of spectroscopic methods of analysis in connection with color-producing reactions is one of the first methods used that had the sensitivity needed for analysis at the part per million (ppm) level. Although developments in colorimetry were gradual, a large number of methods were eventually developed and became the starting point for much of the trace analysis in the first part of the twentieth century. For example, the Gutzeit method was based on the color reaction of generated arsine gas from a sample as it reacted with a strip of treated paper, and it eventually became official for arsenic determination. Schechter et al. (1945) carried out the first practical residue analysis for DDT using colorimetric methods, and these methods of analysis persisted until most were displaced by chromatographic methods.

2.3. Development of Chromatography

Environmental and residue analysis was extremely difficult after organic compounds replaced the arsenicals as pesticides, as the extracted sample would now contain a complex mixture of organic compounds. The primary approach in

such cases would normally be to try to carry out some spot tests for functional groups and hope that there were no serious interferences. The development of chemical separation methods based on chromatography dates at least to the turn of the century and probably before that; no single individual was responsible for its discovery. Adsorption and paper chromatography were in use in the first part of the twentieth century, but although they were quite useful in the purification of compounds on a preparative scale, separation of compounds without the ability to detect what has just been separated does not in itself allow trace analysis. This would later be accomplished by instrumental separation methods in the form of gas and liquid chromatography.

2.4. Instrumental Methods in Organic Trace Analysis

At about the 1920s and 1930s it was widely recognized that the usual gravimetric and volumetric methods in classical quantitative analysis were not sufficiently sensitive as commonly carried out for certain purposes, such as when sample quantity was limited. As a result, the art of ultramicroquantitative analysis gradually developed. This was a scaling down of conventional methods to the point at which quantities well under a microgram could be analyzed. However, the science was not developed to the point of extensive use in organic trace analysis in part because of the long-standing emphasis on the analysis of inorganic substances that dominated quantitative analytical chemistry at the time. Moreover, although very good results can be obtained by ultramicroanalysis, relatively few individuals had the skill and knowledge required (to say nothing of the patience!). It is not easy to advance the practice of a branch of chemistry when the standard deviation is so strongly dependent on the individual making the measurement. For typical applications, refer to a text such as that of Kirk (1950).

One of the earlier applications of an instrumental method to food analysis is the organic halide gas detector of Martinek and Marti (1931). Concerned about the possible presence of methyl chloride (a refrigerant) in air and foods, they developed a flame test based on the change in color of a gas flame in contact with copper (a type of modified Beilstein test).

Mass spectrometry had been developed in the first decade of the twentieth century by J. J. Thomson, but his instrument was not an analytical prototype but rather a device to show that elements could exist as isotopes. (Remember that although chemists in particular often used the atomic theory, there was little direct evidence of the existence of atoms. Much of the evidence fell into place about this time, with Thomson's mass spectrometer, Millikin's oil drop experiment, etc.). An instrument that is more nearly contemporary in application would not come until the 1930s and later.

Polarography was invented by Heyrovsky in the 1920s and later developed into a widely used analytical method for inorganic compounds, but, as noted by Gunther and Blinn (1955), it was not commonly used in residue analysis, perhaps because of excessive background interference.