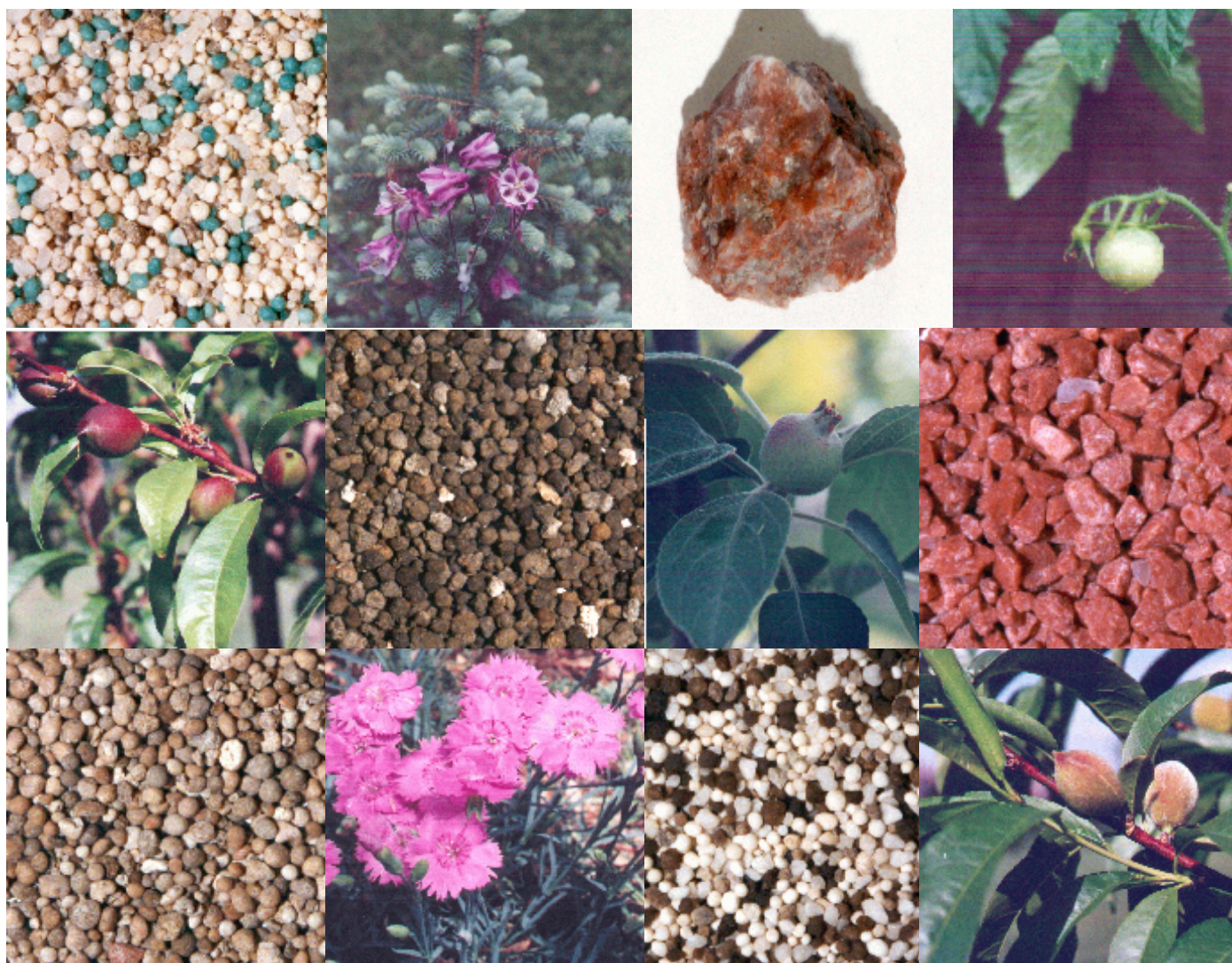




Survey of Fertilizers and Related Materials for Perchlorate (ClO_4^-)

Final Report



Survey of Fertilizers and Related Materials for Perchlorate (ClO_4^-)

Final Report

By

Edward Todd Urbansky
U.S. Environmental Protection Agency
Cincinnati, OH 45268

Timothy W. Collette
U.S. Environmental Protection Agency
Athens, GA 30605

Wayne P. Robarge
North Carolina State University
Raleigh, NC 27695-7619

William L. Hall
IMC-Global
Mulberry, FL 33860

James M. Skillen
The Fertilizer Institute
Washington, DC 20002

Peter F. Kane
Office of Indiana State Chemist and Seed Commissioner
West Lafayette, IN 47907-1154

This study was conducted in cooperation with North Carolina State University, IMC-Global, The Fertilizer Institute, the Office of Indiana State Chemist and Seed Commissioner, and the International Fertilizer Development Center.

National Risk Management Research Laboratory
Office of Research and Development
U.S. Environmental Protection Agency
Cincinnati, OH 45268

Notice

The U.S. Environmental Protection Agency, through the National Risk Management Research Laboratory of its Office of Research and Development, managed and collaborated in the research described here. It has been subjected to the agency's peer and administrative review and has been approved for publication as an EPA document. Mention of trade names or commercial products does not constitute endorsement or recommendation for use. In an effort to save paper and reduce printing costs, this report is being issued by the EPA only as an Adobe Acrobat portable document format (pdf) file. Adobe Acrobat Reader is available free of charge via the Adobe website.

Foreword

The U.S. Environmental Protection Agency is charged by Congress with protecting the nation's land, air, and water resources. Under a mandate of national environmental laws, the agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. To meet this mandate, EPA's research program is providing data and technical support for solving environmental problems today and building a science knowledge base necessary to manage our ecological resources wisely, understand how pollutants affect our health, and prevent or reduce environmental risks in the future.

The National Risk Management Research Laboratory is the agency's center for investigation of technological and management approaches for preventing and reducing risks from pollution that threatens human health and the environment. The focus of the laboratory's research program is on methods and their cost-effectiveness for prevention and control of pollution to air, land, water, and subsurface resources; protection of water quality in public water systems; remediation of contaminated sites, sediments and ground water; prevention and control of indoor air pollution; and restoration of ecosystems. NRMRL collaborates with both public and private sector partners to foster technologies that reduce the cost of compliance and to anticipate emerging problems. NRMRL's research provides solutions to environmental problems by developing and promoting technologies that protect and improve the environment; advancing scientific and engineering information to support regulatory and policy decisions; and providing the technical support and information transfer to ensure implementation of environmental regulations and strategies at the national, state, and community levels.

This publication has been produced as part of the laboratory's strategic long-term research plan. It is published and made available by EPA's Office of Research and Development to assist the user community and to link researchers with their clients.

E. Timothy Oppelt, Director
National Risk Management Research Laboratory

Abstract

The most comprehensive survey of fertilizers and other raw materials for perchlorate to date has been conducted to determine whether these could be significant contributors to environmental perchlorate contamination. The data span a large range of commercial products; however, they were collected over a relatively short time period and comprise a snapshot rather than addressing temporal patterns of perchlorate occurrence. This investigation was designed to account for the difficulties in chemical analysis presented by fertilizer matrices and the problems in obtaining representative samples of these materials. Emphasis was placed on sampling source materials (which also form the basis of most blends) to broaden the applicability of the results to production farming as well as consumer use. Field samples of 48 different products from manufacturers of major commodity chemicals were collected from representative sites around the nation. These covered major sources of macronutrients, some sources of micronutrients, and several sources of fillers/additives. Whenever possible, field samples were collected under supervision of state chemists or agriculture department staff. The field samples were riffled and divided; portions of each material were sent to several laboratories for analysis. Perchlorate was dissolved by leaching the material with deionized water with shaking. Subsequently, the aqueous leachates were subjected to ion chromatography using Dionex IonPac AG16 and AS16 columns. All materials were tested by at least four independent laboratories. Laboratories were required to demonstrate satisfactory recovery of fortifications and performance on 7 quality control samples; agreement on duplicate portions (not identified to the labs) of four materials was also required. Each laboratory had previously been subjected to a performance evaluation using test samples. Except for those products derived from Chilean caliche (a natural perchlorate source), the specific natures of the manufacturing processes suggest that perchlorate should not be present in most fertilizers. Chilean nitrate salts constitute about 0.14% of U.S. fertilizer application. Perchlorate was positively detected only in those materials known to be derived from Chilean caliche. The data obtained here fail to suggest that fertilizers contribute to environmental perchlorate contamination other than in the case of natural saltpeters or their derivatives. Limited discussion is included on the implications for agriculture and horticulture as well as factors that complicate investigations or data analysis and interpretation.

Contents

Notice	ii
Foreword	iii
Abstract	iv
Contents	v
Tables and figures	vi
1 Environmental perchlorate: what role for fertilizer?	1
1.1 Introduction	1
1.2 Fertilizer manufacture and use	1
1.2.1 Nutrient availability	1
1.2.2 Nitrogen sources	2
1.2.3 Phosphate sources	5
1.2.4 Potassium sources	5
1.2.5 Information sources	6
1.3 Previous fertilizer analysis studies	7
2 Survey of fertilizers and related materials	9
2.1 Objectives	9
2.2 Phase 1—Evaluation of laboratories	9
2.3 Phase 2—Analysis of samples	10
2.3.1 Sampling and analysis strategy	10
2.3.2 Results	11
2.3.3 Discussion	11
3 Implications for vascular plants	18
3.1 Introduction	18
3.2 Complicating factors	18
3.2.1 Chemical influences on ion transport	19
3.2.2 Concentration	19
3.2.3 Tissue-specific accumulation	20
3.2.4 Soil sorption	20
3.2.5 Summary	20
3.3 Difficulties in analysis	21
3.4 Implications of perchlorate absorption and accumulation	21
References	23

Tables and Figures

Tables

1.1	Some common agricultural fertilizers used in production farming	2
1.2	Consumption (in tons) of nitrate salts in regions of the continental United States for the year ending June 30, 1998	4
1.3	Annual consumption/application (in tons) of some nitrogen fertilizers for several states	4
1.4	Annual production (tonnage) of nitrate salts by some manufacturers who supplied the U.S. marketplace	5
2.1	Fertilizers and related materials surveyed for perchlorate	13
2.2	Summary results for perchlorate concentration detected by replicate analyses of samples listed in Table 2.1	15
2.3	Tested fortifications (spikes) and recoveries in solutions of samples listed in Tables 2.1–2.2	17

Figures

1.1	Schematic of urea production	2
1.2	Synthesis of nitric acid by the redox reaction of ammonia and atmospheric oxygen	4
1.3	Schematic of ammonium nitrate production	4
1.4	Operational schematic of phosphate rock processing	5
1.5	Bucketwheel used in mining phosphate rock	5
1.6	Agricultural DAP	5
1.7	The mineral sylvite (KCl)	6
1.8	Canadian potash mines can be kilometers below the surface	6
1.9	Sylvite and sylvinitite can be mined by dissolving the minerals in the water and pumping the brine to the surface	6

Acknowledgments

We acknowledge the following individuals and institutions for their assistance in the completion of this project. This includes the services of participating laboratories, state regulatory agencies, and industry employees.

Jay Johnson & Kent W. Richman
American Pacific Corporation
Cedar City, Utah

Stanley Kobata, Harry Welte & Paul Roos
California Department of Food and Agriculture
Sacramento, California

Thomas E. Carville, Carol F. Schexnaydor & Jesús I. Peralta
CF Industries
Donaldsonville, Louisiana, and Washington, D.C.

D.H. Thomas, P.E. Jackson & J.S. Rohrer
Dionex Corporation
Sunnyvale, California

Catherine A. Kelty, Stephanie K. Brown, Matthew L. Magnuson, J.
Jackson Ellington & John J. Evans
U.S. Environmental Protection Agency
Cincinnati, Ohio, and Athens, Georgia

David F. Graves & John B. Sargeant
Florida Department of Agriculture and Consumer Services
Tallahassee, Florida, and Lakeland, Florida

Steve Gamble
IMC-Kalium
Carlsbad, New Mexico

Linda Weber, David Gadsby, Bonnie Lingard,
Daphne Williams, Charles Kinsey, Julie Thompson,
Pam Burgess & Dennis Sebastian
IMC-Phosphates Environmental Laboratory
Bradley, Florida

George A. Kennedy, Celia G. Calvo, Bobby W. Biggars,
& Steven J. Van Kauwenbergh
International Fertilizer Development Center
Muscle Shoals, Alabama

Ali Haghani and Andrew Eaton
Montgomery Watson Laboratories
Pasadena, California

Tina Sack
New Mexico Department of Agriculture
Roswell, New Mexico

Michael Hancock
Office of Indiana State Chemist and Seed Commissioner
West Lafayette, Indiana

George W. Latimer
Office of Texas State Chemist
College Station, Texas

Guillermo Ramirez
North Carolina State University
Raleigh, North Carolina

Baohua Gu
Oak Ridge National Laboratory
Oak Ridge, Tennessee

Richard A. Beidelschies
Ohio Department of Agriculture
Reynoldsburg, Ohio

B.H. James, A.A. Coe & Ray Poole
PCS Phosphate
Aurora, North Carolina

Gene H. Williams & Sanford Simon
Pursell Industries
Orrville, Ohio, and Birmingham, Alabama