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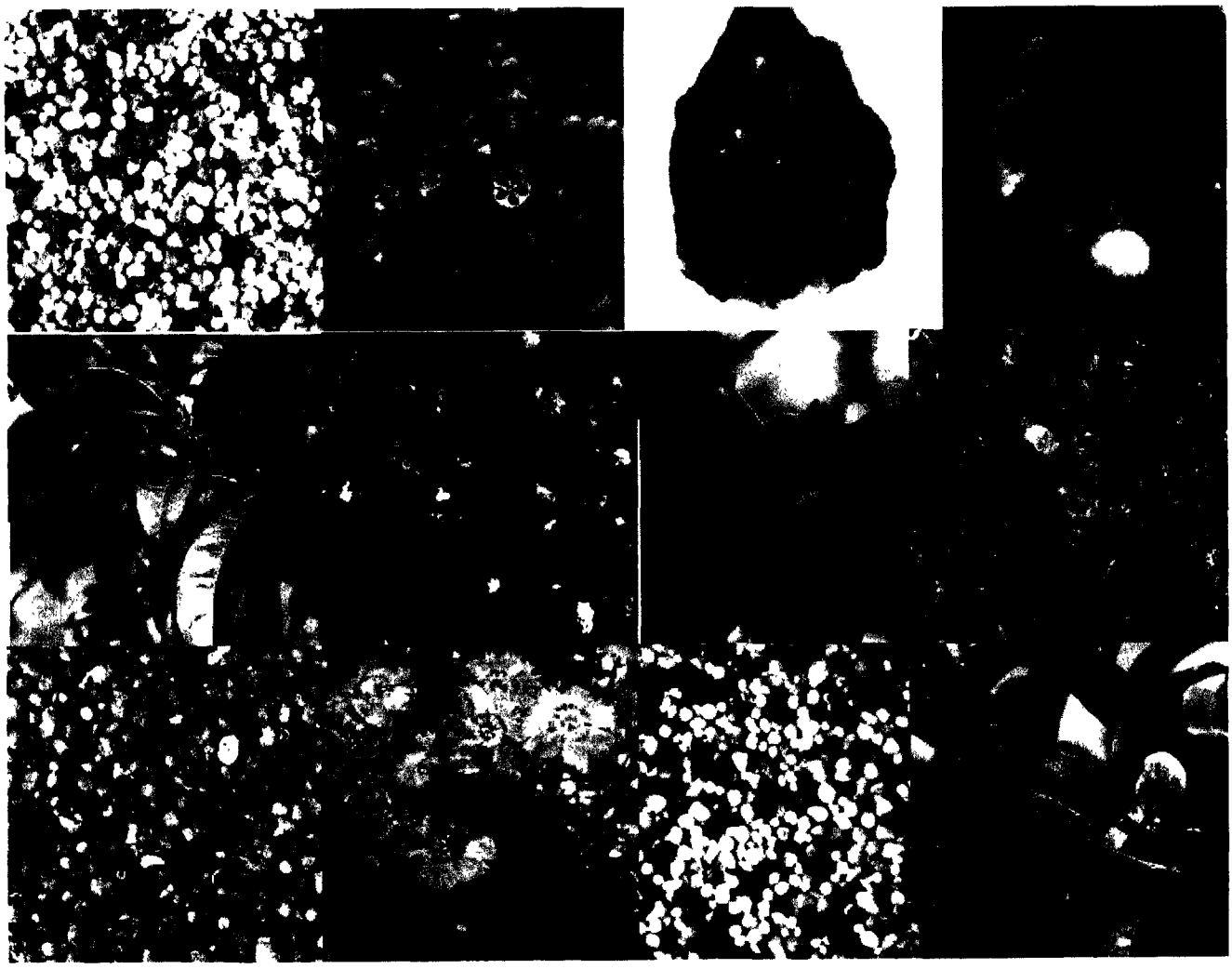
Survey of Fertilizers and Related Materials for Perchlorate (ClO_4^-)

Final Report



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

Final Report

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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
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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

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 sylvinite can be mined by dissolving the minerals in the water and pumping the brine to the surface 6

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Chapter 1
Environmental perchlorate: what role for fertilizer?

1.1. Introduction

Perchlorate was discovered in U.S. waterways in the late 1990s. Most perchlorate salts are used as solid oxidants or energy boosters in rockets or ordnance; therefore, much of the perchlorate-tainted waterways in the U.S. can be traced to military operations, defense contracting, or manufacturing facilities. Perchlorate ion is linked to thyroid dysfunction, due to its similarity in ionic radius to iodide (Clark, 2000). Because perchlorate-tainted waters are used for irrigation, there are questions about absorption, elimination, and retention in food plants. Furthermore, recent reports have suggested that fertilizers could represent another source of perchlorate in the environment. Sporadic findings of perchlorate in fertilizers were initially alarming because of the widespread use of fertilizers in production farming. Because of the dependence of U.S. agriculture on chemical commodity fertilizers, it was clear that assessment of any possible role of fertilizers would require investigation.

Attention has been drawn to the possible roles of fertilizers in environmental perchlorate contamination for two reasons. First, perchlorate-tainted agricultural runoff could lead to pollution of natural waterways used as drinking water sources. Second, there is a potential for food plants to take up soluble compounds—including perchlorate salts—and thus provide an alternate route of exposure. It has long been known that Chile possesses caliche ores rich in sodium nitrate ($NaNO_3$) that coincidentally are also a natural source of perchlorate (ClO_4^-) (Schilt, 1979; Ericksen, 1983). The origin of the sodium perchlorate ($NaClO_4$) remains an area of debate, but it is nonetheless present and can be incorporated into any products made from the caliche.

1.2. Fertilizer manufacture and use

American farmers apply about 54 million tons of fertilizer yearly. As with many commodity chemicals, large scale purchases are dictated by cost of raw materials, which are in turn normally influenced by transportation costs. Thus, proximate (rather than distant) sources of agricultural chemicals are likely to play the greatest roles in local ecosystems involved in production farming. In addition, processing aids (e.g., clays) are likely to be derived from the closest possible source. Production farming relies on cheap and available sources of primary plant nutrients (macronutrients): nitrogen, phosphorus, and potassium. Fertilizer grades (or guaranteed analyses) are expressed using the convention of Samual Johnson, a student of Justus Liebig, who has been called the "father of the fertilizer industry." In the Johnson convention, nitrogen is expressed as a mass fraction (weight percent) as it was originally determined by the Kjeldahl method. Phosphorus and potassium are denoted in terms of the minerals formed by ashing at high temperature. Thus, phosphorus is expressed as the mass fraction of the empirical formula of its oxide, diphosphorus pentoxide (P_2O_5), and potassium is expressed as the mass fraction of its oxide, potassium oxide (K_2O). This nomenclature does not reflect the actual composition of the fertilizer, however, nor current practice in assaying it.

1.2.1. Nutrient availability

To minimize the need for multiple applications and to prevent overdosing, timed-, delayed-, or controlled-release fertilizers are used in both agricultural and horticultural applications. There are two mechanisms to delay nutrient release. The first is to use essentially insoluble minerals that are not readily converted to absorbable aqueous phase nutrients, for example phosphate rock or other calcium phosphates. The second is to coat the soluble fertilizer with an insoluble material, such as a urea-based polymer or sulfur. This is often done with consumer products, e.g., lawn fertilizers. Most urea-based polymers are methylene ureas or urea-methanal blends. As urea polymers are hydrolyzed, they too serve as a source of nutrients.

Many commodity chemicals used as agricultural fertilizers contain fairly high concentrations of one, or sometimes two, of the primary plant nutrients (Table 1.1). Trace metals (e.g., boron, copper, magnesium) can be applied separately or along with these primary nutrients on a farm site. Fertilizer application in production farming is highly dependent on the crop and the native soil. Crops are influenced by climate, weather, topography, soil type, and other factors that are generally similar within a geographical region; therefore, crops and fertilizer use are also similar within such a region. This is of course unsurprising and consistent with agricultural production of dairy foods, corn, tobacco, wheat, etc. Because all plants require the same primary nutrients, there is some usage to provide these regardless of crop. Local soil conditions also dictate what nutrients should be augmented, and there can be large regional variations.

Table 1.1. Some common agricultural fertilizers used in production farming†

Chemical name	Chemical formula	Grade (N-P-K ratio)
Ammonia (anhydrous)	NH_3	82-0-0
Ammonium nitrate	NH_4NO_3	34-0-0
Urea	$(NH_2)_2CO$	46-0-0
Ammonium monohydrogen phosphate (diammonium phosphate)	$(NH_4)_2HPO_4$	18-46-0
Potassium chloride (pure)	KCl	0-0-62
Potassium magnesium sulfate	$K_2Mg_2(SO_4)_3$	0-0-22
Triple superphosphate	$Ca(H_2PO_4)_2 \cdot H_2O$*	0-46-0

†Most solid fertilizers contain processing aids (e.g., clays) that keep the product from becoming a solid mass. Granular products are often dusted with these. *Triple superphosphate is a somewhat ill-defined substance, being a slightly hydrous mixture of calcium hydrogen phosphates (variable protonation). It is represented here as calcium dihydrogen phosphate monohydrate, but that compound is the main component and not the only component.

On the other hand, consumer products can be distributed over larger geographical regions because of the nature of the market. For example, major manufacturers have a limited number of sites dedicated to blending multiple-nutrient formulations. These products are often sold as bagged fertilizers through home-improvement centers, nurseries, florists, horticulturists, and department (or other retail) stores. Unlike agricultural fertilizers, consumer products are usually multi-nutrient formulations. In addition, trace metals are sometimes incorporated directly into them. Because the average user will apply only a very small amount of trace metals (or even primary nutrients) relative to a production farm, it is more economical, more practical, and more convenient to use multiple-nutrient formulations. Moreover, the average consumer does not have the wherewithal to disperse careful doses of several single-component fertilizers at the appropriate times of the growing season.

Multiple-component fertilizers can be timed (controlled) release or soluble blends. Many multiple-component products are intended for soil amendment to lawns or gardens, e.g., 10-10-10, and other common multiple-macronutrient formulations. Water-soluble blends are used to supply nutrients rapidly to growing plants and are generally applied repeatedly during a growing season (as with each watering), whereas timed-release fertilizers allow water to leach nutrients slowly for release to the soil and plants. They are applied perhaps once or twice a year, e.g., a lawn winterizer. Obviously, soluble and insoluble fertilizers cannot be entirely identical chemically. However, the distinction is essentially irrelevant for agricultural fertilizers, which are applied to fortify particular nutrients. Of course, allowances must be made for the bioavailability of these nutrients. As a general rule, agricultural fertilizers are soluble chemicals. Because fertilizer application on production farms is geographically delimited, there is considerable interest in knowing which commodity chemicals might contain perchlorate and how much. Such information might suggest regions for further investigation. Moreover, it will be important to know what crops might potentially be affected—if any.

1.2.2. Nitrogen sources

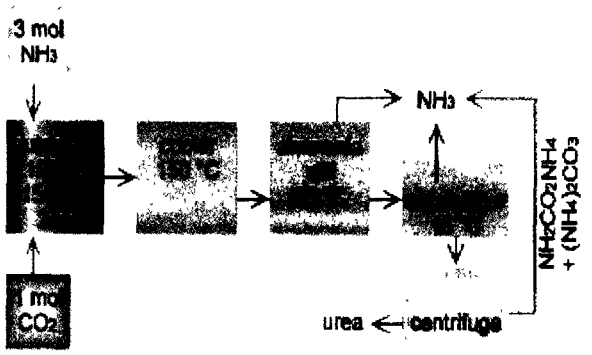

Figure 1.1. Schematic of urea production.

The simplest nitrogen source is anhydrous liquid ammonia. Liquid ammonia is stored in bulk tanks and injected directly into the soil. No fertilizer has a higher nitrogen content. Ammonia is made using the Haber process, which entails heating desiccated nitrogen (separated from liquified air) and hydrogen (usually from methane) in the presence of a catalyst at 500-700 °C.

Urea is also a common source of nitrogen. Highly soluble in water, urea hydrolyzes to carbonic acid and ammonia, given time. The industrial process used to synthesize urea is shown in Figure 1.1. In addition to its use as a fertilizer, a special feed grade of urea is used to supplement cattle feed.

Nitrate salts are also used as fertilizers. Ammonium nitrate is the primary nitrate salt used in production farming. Most—if not all—ammonium nitrate today is made from atmospheric gases. None of the major nitrogen fertilizer producers [Potash Corporation of Saskatchewan (PCS), Agrium, Coastal, Mississippi Chemical, Kemira Dansmark, and IMC] use natural saltpeters in manufacturing. IMC and PCS do not sell nitrate-based fertilizers, focusing instead on urea, ammonium phosphates, and similar nitrogenous compounds. Consequently, perchlorate contamination is not possible from the raw materials. Ammonium nitrate is prepared from nitric acid and ammonia. Nitric acid is manufactured by the process shown in Figure 1.2. Ammonium nitrate is produced as shown in Figure 1.3.

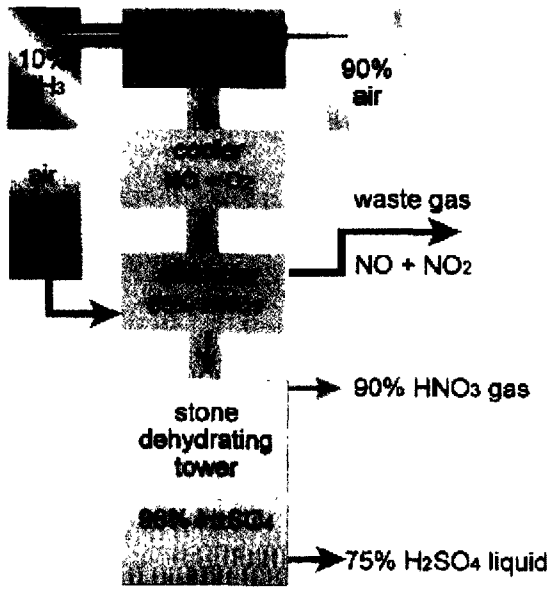

Figure 1.2. Synthesis of nitric acid by the redox reaction of ammonia and atmospheric oxygen. A 1:9 ratio of ammonia and air pass through Rh/Pt gauze. The cooled nitric oxide and oxygen pass into an absorber where more air is added and the NO is converted to nitrogen dioxide. The nitrogen dioxide undergoes hydrolytic disproportionation to give nitric acid with NO as a byproduct. After dehydration, the nitric acid vapor is recovered from the gas phase.

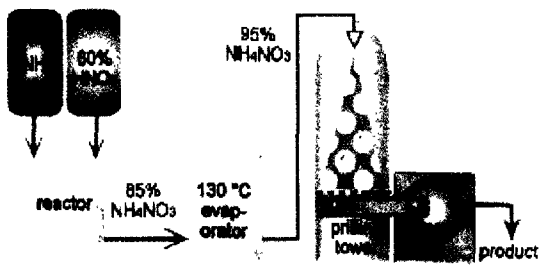

Figure 1.3. Schematic of ammonium nitrate production. Aqueous nitric acid and anhydrous ammonia are combined to produce the salt, which is then prilled and dried.

The alkali metal saltpeters (sodium and potassium nitrates) are also used as nitrogen sources. Their mineral forms are known as soda niter (nitratine) and potash niter (nitrine), respectively. Chile saltpeter ($NaNO_3$) is mined from caliche ores in the North. The mined rock contains veins rich in sodium nitrate. The ore is crushed and mixed with water to dissolve the soluble salts. The sodium nitrate is then recovered from the leachate. Chile's Sociedad Quimíca y Minera S.A. (SQM) reports annual production of about 992,000 tons of nitrate products. SQM North America sold some 75,000 tons to U.S. farmers in 1998. The company touts its products primarily for cotton, tobacco, and citrus fruits. It is the caliche ores that contain naturally occurring perchlorate. No other company sells a product derived from caliche as of this writing; however, Potash Corporation of Saskatchewan does own caliche mines in Chile (Searls, 1999; EIU, 1999)

Because nitrate salts (saltpeters) find use as fertilizers, these natural resources have been mined and refined to produce commercial fertilizers for domestic use or for export. Chilean nitrate fertilizers ($NaNO_3$ and KNO_3) are manufactured by SQM. SQM markets its products in the U.S. under the name Bulldog Soda. Chilean nitrate salts are sold to agricultural operations, chemical suppliers, and consumer-oriented companies such as Voluntary Purchasing Groups, Inc., or A.H. Hoffman, Inc., who repackage and resell it as Hi-Yield® or Hoffman® nitrate of soda, respectively. Also, secondary users may incorporate Chilean nitrate salts into water-soluble plant foods, lawn fertilizers, and other retail (specialty) products.

Due to their cost and availability, Chilean nitrates are niche fertilizers. SQM markets its products to growers of tobacco, citrus fruits, cotton, and some vegetable crops, particularly emphasizing that the products are low in chloride content (CNC, 1999). As noted above, typical American fertilizer consumption is 54 million tons per year; consequently, most U.S. fertilizers are derived from other raw materials. For example, ammonium nitrate (NH_4NO_3), which is often used for purposes similar to $NaNO_3$, is manufactured from methane, nitrogen, and oxygen. There is no evidence that any ammonium nitrate is derived from Chilean caliche. On account of its low usage, perchlorate from Chilean nitrates cannot represent a significant anthropogenic source of perchlorate nationwide, regardless of the perchlorate content. Recent examination of two manufacturing lots found perchlorate concentrations below 2 mg g^{-1}, i.e., < 0.2% w/w, with some lot-to-lot variability (Urbansky, 2001). However, in a recent letter to EPA, SQM North America's President Guillermo Farias indicated that SQM had modified its refining process to produce fertilizer containing less than 0.01% perchlorate (<0.1 mg g^{-1}); this corresponds to a reduction of 90-95%. SQM monitors its production stream every 2 hours to verify the perchlorate concentration. Accordingly, previous data on perchlorate content are only applicable in a historical sense rather than being reflective of ongoing fertilizer use.

As Table 1.2 indicates, there is limited application of natural saltpeters as fertilizers in the U.S. based simply on total consumption. There just is not enough production of the natural materials. Some states keep detailed records on fertilizer use, especially of chemical commodities used in production farming, but others do not. For example, the Office of Indiana State Chemist is required to keep track of only the top ten fertilizers; even ammonium nitrate is not among the top ten in Indiana. As a result, it is not easy to discern the potential distribution of minor fertilizers known to contain traces of perchlorate salts. Table 1.2 gives the tonnage for a few nitrogen fertilizers for several states. Many states do not keep records as detailed as those of the Office of the Texas State Chemist, which tracks each fertilizer by grade (N-P-K ratio) and tonnage. The Corn Belt relies heavily on urea

and anhydrous ammonia as nitrogen sources, as shown by Indiana and Ohio consumption of these two chemicals in Table 1.3, while ammonium nitrate finds greater use in tobacco-farming states.

Table 1.2. Consumption (in tons) of nitrate salts in regions of the continental United States for the year ending June 30, 1998

Region	NH_4^+	Na^+	K^+	Na^+/K^+
New England	2,469	194	142	0
Mid-Atlantic	33,556	260	12,064	0
South Atlantic	162,035	14,870	17,308	21,762
Midwest	81,585	189	1,496	5
Great Plains	436,371	409	296	55
East South Central	489,603	7,786	2,122	914
West South Central	338,618	4,192	652	2,851
Rocky Mountain	254,168	831	9,022	0
Pacific	148,340	10,281	146	0
U.S. Total*	1,946,868	39,013	46,100	22,762

Key: New England (ME, NH, VT, MA, RI, CT); Mid-Atlantic (NY, NJ, PA, DE, MD, WV); South Atlantic (VA, NC, SC, GA, FL); Midwest (OH, IN, IL, MI, WI); Great Plains (MN, IA, MO, ND, SD, NE, KS); East South Central (KY, TN, AL, MS); West South Central (AR, LA, OK, TX); Rocky Mountain (MT, ID, WY, CO, NM, AZ, UT, NV); Pacific (CA, OR, WA); *Total U.S. includes HA, AK, PR. Source: Association of American Plant Food Control Officials/The Fertilizer Institute, *Commercial Fertilizers 1998*. D.L. Terry and B.J. Kirby, Eds. University of Kentucky: Lexington, KY, 1998.

Sodium and potassium nitrates make up a small fraction of the nitrate application in the United States; however, prior to the establishment of nitric acid and ammonia factories, natural saltpeters played significant roles in American agriculture. In addition, ammonium nitrate was manufactured from Chile saltpeter before the industrialized oxidation of ammonia to nitric acid became commonplace in the 1940s. Decades ago, ammonium nitrate was prepared from Chilean sodium nitrate by ion exchange rather than from gaseous reactants. Historical use of ammonium nitrate previous to or in the first half of the 20th century might be linked to contaminated groundwater, and has been attributed to one manufacturing facility in Arizona (EPA, 1999). On the other hand, a recent survey of water supplies for perchlorate was unable to detect perchlorate in nearly all of them, and concluded that perchlorate contamination is generally localized and related to point sources (Gullick, 2001). Reliable data on the use of natural saltpeters appear to be unavailable. While most nitrate salt manufacturers rely on ammonia oxidation (Table 1.4), which is a chlorine-free process, the possibility of contamination from products derived from Chile saltpeter cannot be ignored.

The lack of information on natural attenuation as well as limited knowledge of hydrogeology makes it difficult to determine where and how such problem sites might be found. For this reason, monitoring for perchlorate under the EPA's Unregulated Contaminant Monitoring Rule for drinking water can be expected to provide some of the most useful information. Meanwhile, it is instructive to consider the processes by which major nutrients are produced so as to evaluate the possibilities for contamination.

Table 1.3. Annual consumption/application (in tons) of some nitrogen fertilizers for several states

State	$NH_3^{\bullet}$ 82-0-0	Urea 46-0-0	NH_4NO_3 34-0-0	KNO_3 14-0-46
Arkansas*	1,207	465,737	62,003	N.R.†
Georgia□	3,859	15,084	56,215	N.R.
Indiana*	193,347	48,478	N.R.	N.R.
Maryland§	1,155	11,614	9,518	N.R.
New Mexico⁺	13,747	34,348	2,725	N.R.
Ohio*	86,499	115,180	7,516	N.R.
Texas**	142,383	74,235	80,120	1,115
West Virginia⁺	390	4,476	1,283	N.R.

•Anhydrous. *1998. §July 1998–June 1999. ⁺1997. **March–August 1998. †N.R. = not reported. □July 1998–June 1999. Sources: Arkansas State Plant Board; Association of American Plant Food Control Officials; Plant Food, Feed, & Grain Division, Georgia Department of Agriculture; Office of Indiana State Chemist and Seed Commissioner; Maryland Department of Agriculture, Office of Plant Industries and Pest Management, State Chemist Section; Feed, Seed, and Fertilizer Bureau, New Mexico Department of Agriculture; Office of the Texas State Chemist; West Virginia Agricultural Statistics Service.

Table 1.4. Annual production (tonnage) of nitrate salts by some manufacturers who supplied the U.S. marketplace*

Company	ammox† KNO_3	ammox $NaNO_3$	ammox NH_4NO_3	ammox HNO_3	Chilean $NaNO_3$	Chilean KNO_3
Agrium§ Calgary, Alberta, Canada	np¶	np	630,000	np	546‡	652‡
Coastal Chem, Inc. Cheyenne, WY§§	np	np	306,180	245,164	np	np
Kemira Danmark§ Fredericia, Denmark	3239	np	np	np	np	np
Vicksburg Chemical Co.§ Vicksburg, MS	151,000	np	np	np	np	np

*Anumber of companies with smaller production outputs make NH_4NO_3 and urea, such as Apache Nitrogen Products Inc., which manufactured 50,000 tons of fertilizer in 2000. This table excludes sales from SQM.†The term "ammox" refers to use of ammonia oxidation to produce nitric acid. §Actual or estimated production for 2000. ¶The designation "np" means that the manufacturer reported to EPA that this material was not a product. ‡This material was sold by Western Farm Services, an Agrium subsidiary, and was reported to have "little to no detectable perchlorate" according to information provided by Agrium to EPA. §§Actual production for 1999.

1.2.3. Phosphate sources

Phosphate rock is mined in a number of states, including Florida, Idaho, and Montana. Florida's phosphate rock deposits are near the surface (~8 m down) and formed 5-15 million years ago. They are obtained by removing the overburden (covering rock). Figure 1.4 shows phosphate rock processing. In North Carolina, overburden is taken up via bucketwheel (Figure 1.5). Natural phosphate rocks usually contain a mixture of the apatite minerals. Fluoroapatite has the empirical formula $Ca_5(PO_4)_3F$.

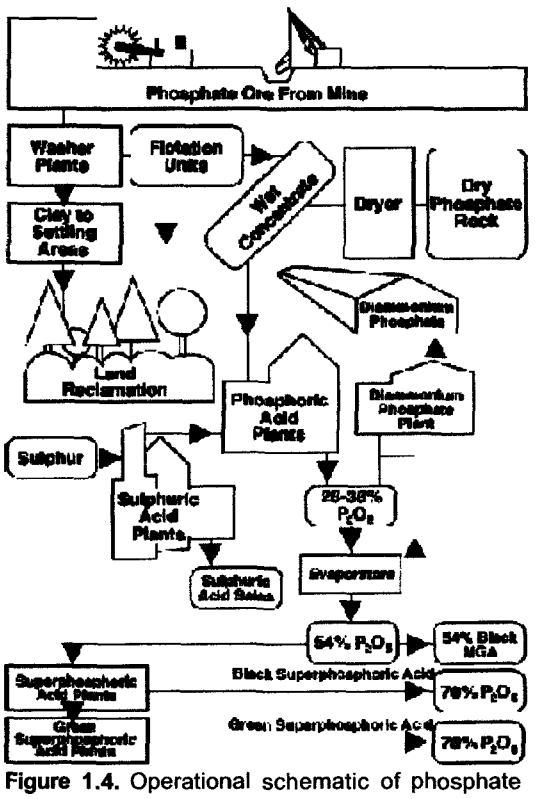

Figure 1.4. Operational schematic of phosphate rock processing. MGA refers to merchant grade acid. © PCS Phosphate. Used with permission.

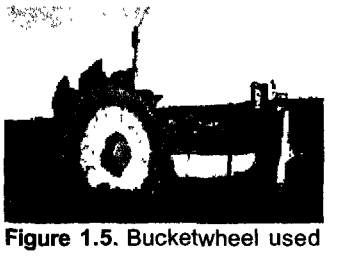

Figure 1.5. Bucketwheel used in mining phosphate rock. Photo © PCS Phosphate. Used with permission.

Ammonium monohydrogen phosphate, $(NH_4)_2HPO_4$, is commonly referred to as DAP in the agricultural chemical industry, short for diammonium phosphate. DAP is a source of both nitrogen and phosphorus and has a grade of 18-46-0. The ACS reagent is a white crystalline material; NIST sells J.T. Baker Ultrex ammonium monohydrogen phosphate as SRM 694 for use by fertilizer manufacturers in assaying this material. However, agricultural DAP is generally a mixture of gray, brown, and/or black pellets (Figure 1.6). Some of this color is due to residual calcium minerals (e.g., apatites, gypsum) and some is due to natural organic matter. Most agricultural DAP contains 6-15 mol% $NH_4H_2PO_4$ or monoammonium phosphate (MAP).

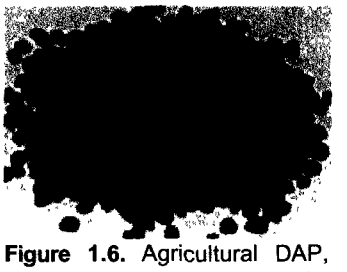

Figure 1.6. Agricultural DAP, product provided courtesy of CF Industries.

In the Corn Belt, granular triple superphosphate or GTSP (0-46-0) and DAP, dominate the market. About 82% of the *ortho*-phosphoric acid produced in the U.S. goes into fertilizer manufacture, with 49% into DAP and 10% into MAP.

Figure 1.7. The mineral sylvite (KCl). The red or brown color comes from occluded hematite (Fe_2O_3) or limonite ($Fe(O)OH{\cdot}nH_2O$). Materials provided courtesy of Kova, Inc., (left) and CF Industries, Inc. (right).

1.2.4. Potassium sources

Essentially no potash (K_2O/K_2CO_3) is used as a fertilizer today, but many products are referred to as potash for historical reasons. Potassium nitrate and potassium chloride (muriate of potash, MOP) dominate this market. Sylvite (KCl) is mined in Canada, and is the most popular potassium source in the Corn Belt. Both Saskatchewan and New Brunswick have sylvite and/or sylvinite mines. The red material on the left in Figure 1.7 has a guaranteed analysis of 0-0-60, while the purer material on the right is guaranteed at 0-0-62, which represents the maximum, within the limits of experimental error.

Sylvinite (43% KCl, 57% NaCl) deposits occur in New Mexico and can be refined to remove much of the halite (NaCl). New Mexico also has reserves of sylvite and langbeinite [potassium magnesium sulfate, $K_2Mg_2(SO_4)_3$ or $2K_2SO_4{\cdot}MgSO_4$]. Langbeinite is popular in dairy country as a source of magnesium.

Like Chile saltpeter, these minerals are marine evaporites resulting from the drying up of terminal inland seas. In most cases, deposits of sylvite are hundreds or thousands of meters below the surface, having been covered over by sedimentary rock formations over some 300 million years.

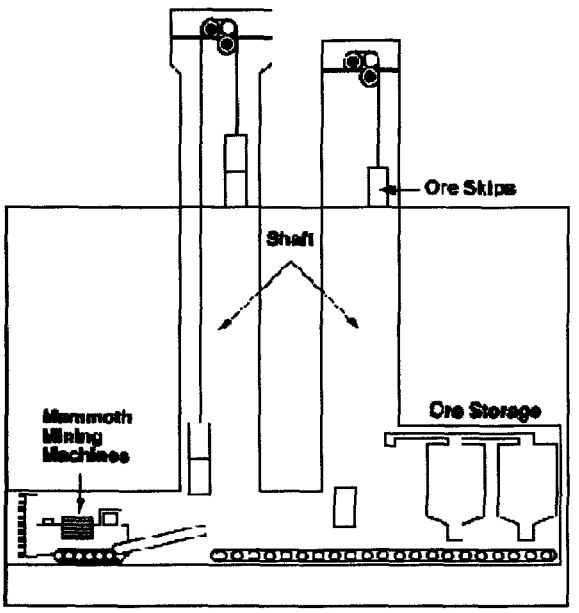

Figure 1.8. Canadian potash mines can be kilometers below the surface. © PCS Potash. Used with permission.

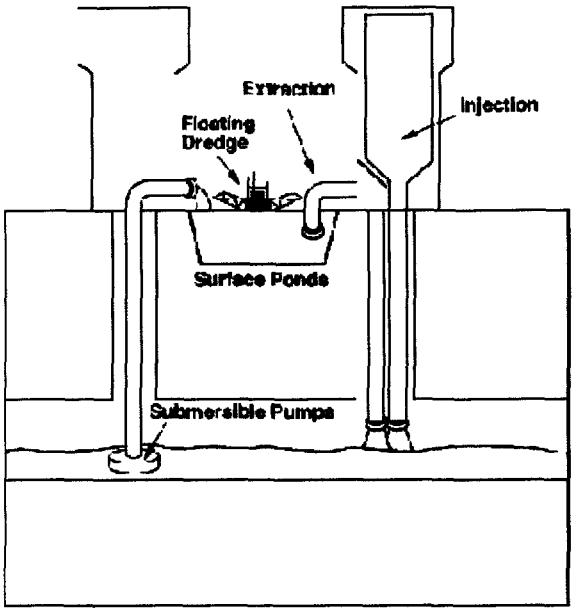

Figure 1.9. Sylvite and sylvinite can be mined by dissolving the minerals in water and pumping the brine to the surface. © PCS Potash. Used with permission.

The market is dominated by two producers, IMC-Kalium and PCS. PCS has deep mines that rely on traditional techniques (Figure 1.8) and solution mines that make use of the solubility of the minerals (Figure 1.9).

1.2.5. Information sources

Information on fertilizer production and application comes from a variety of sources, including trade organizations, manufacturers, and government (state/federal) agencies. Both the U.S. Census Bureau and the U.S. Geological Survey track fertilizer commodities. The Census Bureau's Economics and Statistics Administration publishes an annual report (MA325B, formerly MA28B) as well as quarterly reports (MQ28B) on inorganic fertilizer materials and related products. The Geological Survey publishes reports on fertilizer minerals that cover manufacture, use, regulation, litigation, and other matters (Cf. Lemons 1996; Searls, 1999). Natural Resources Canada also publishes a minerals yearbook (Cf. Prud'homme, 1998). Most publications are available online.

Because data are obtained through many sources, it is common for there to be inconsistencies as well as apparent inconsistencies. Apparent inconsistencies sometimes stem from how materials are tracked. For example, an apparent inconsistency in the data between Tables 1.2 and 1.4 relates to ammonium nitrate production (~940,000 tons) versus consumption (1.8 million tons). However, Table 1.4 neither includes all manufacturers, nor product blends. In addition, the tables do not account for normal fluctuations in inventory. In other

words, a material produced in one year may be sold or used the following year. Taken together, these factors increase the difficulty in monitoring the application of or tracking transactions involving perchlorate-containing materials.

1.3. Previous fertilizer analysis studies

Aside from the analyses of Chilean caliche, there were no studies to suggest that any other processed fertilizer or raw material might contain perchlorate prior to 1998. That year the Ecosystems Research Division of the EPA's National Exposure Research Laboratory (EPA-ORD-NERL-ERD) found perchlorate in several samples that were not derived from Chile saltpeter (Susarla, 1999D). This finding was later duplicated by other investigators from the North Carolina State University Department of Soil Science. However, the presence of perchlorate could only be confirmed in consumer products, and not in agricultural fertilizers. Moreover, subsequent analyses of different bags (likely different lots) of many of the same brands and grades did not show perchlorate (Susarla, 2000; Williams, 2001). The choice of fertilizers is problematic because the same raw materials may be used in a variety of products at a point in time. Additionally, a few major companies are responsible for making a large number of products under several brand names. Furthermore, some companies rely on toll manufacturing so that the products are actually made by another company to meet a specific formulation. Accordingly, an error or contamination associated with one raw material could affect a variety of products without regard to company or application. Since those early days, each subsequent study on fertilizer has attempted to address more issues, and study designs have been continually refined based on what was learned in previous investigations.

The EPA-ORD-NERL-ERD study brought to light a number of important issues for trace analysis of fertilizers. First, most of the research on determining perchlorate to that time had been focused on either finished potable water or raw source water (Urbansky, 2000F). Second, fertilizers are considerably more complicated matrices than dilute water solutions. Third, solid fertilizers are not homogeneous. In fact, some are macroscopically heterogeneous, for example, multi-component formulations used as lawn and garden fertilizers. It is possible to sort out the particles by hand. Thus, representative sampling becomes a key issue. Fourth, the effectiveness of the leaching step must be evaluated. Fifth, the materials must be carefully selected to properly reflect the market of interest, e.g., production farming, lawn treatment, vegetable gardens, houseplant foods.

About the same time as the EPA-ORD-NERL-ERD study, the U.S. Air Force Research Laboratories (AFRL) performed a study to assess interlaboratory corroboration, that is, the ability of different labs to analyze the same sample and get the same result (Eldridge, 2000). Samples of a variety of lawn and garden fertilizers were selected from around the country. The AFRL study used a number of products. These included four brand name products from New York, three from Missouri, and one from California. Overall, these represented multiple lots of four brand name fertilizer products, with some different lots of the same products coming from different cities. The AFRL study did not account for the sources of the commodity chemicals blended into these products, and it did not link manufacturing lots with lots of raw materials. Even bagged fertilizers from different manufacturing lots may be comprised from some of the same raw materials. Therefore, limitations in choice of products prevent extrapolating the results to large scale fertilization (as in production agriculture).

An AFRL contractor was tasked with leaching or dissolving the materials and parceling out the liquid samples to 7 laboratories running IC and 3 using other techniques (capillary electrophoresis, tetraphenylstibonium titrimetry, and Raman spectrometry). Each laboratory was sent a sample of the same test solution for analysis. Laboratories were permitted to use any means of analysis. Ion chromatography, capillary electrophoresis, titrimetry, and Raman spectrometry were all employed. Interlaboratory agreement was generally good, indicating that laboratories were able to determine perchlorate in the fertilizer solutions, despite matrix complexity. Quality control checks were limited to performance on deionized water blanks and perchlorate solutions prepared from deionized water; laboratories were not required to show performance on fortified samples (spike recovery). Some of the samples failed to show Raman scattering lines consistent with their major components; this matter was not addressed.

While interlaboratory agreement was good on the liquid solutions, values for leachates derived from different samples of the same lot of material varied substantially in some cases. Heterogeneity of bagged fertilizer products (especially multiple component products) was therefore demonstrated to be a significant matter by the AFRL study.[1] Specifically, duplicate samples of solid from bagged fertilizers gave aqueous leachates with considerable differences in measured perchlorate concentration: 5.8 ± 0.5 mg g^{-1} versus 2.8 ± 0.3 mg g^{-1} for one product and 0.98 ± 0.14 mg g^{-1} versus 2.7 ± 0.3 mg g^{-1} for another [values here are the average and estimated standard deviation for 10 results (each of which is an average for one of 10 methods]. Such variation may be attributable to sampling error and does not necessarily reflect an actual difference. EPA-ORD-NERL-ERD has observed even wider variation in grab samples, with some measured concentrations as much as 5-7 times larger than others. When some of the same products were subjected to sampling scheme intended to yield a more representative sample, considerably lower intersample variability was observed (Williams, 2001). Less striking variation in perchlorate distribution within and among bags of sodium nitrate fertilizer has been seen for small grab samples of solids, but can be eliminated by more rigorous sampling or by choosing larger sample sizes (Urbansky, 2001).

For one product in the AFRL study, perchlorate concentrations in the first solid sample taken were below the detection limit in one

[1]Here, we call these products bagged fertilizers even though some are sold in boxes or jars; this contrasts with bulk fertilizers sold by railway car or truck and then used for agricultural purposes (or eventually incorporated into a bagged fertilizer). Such products are usually referred to as specialty fertilizers within the industry. While some products are specifically manufactured so as to assure uniform distribution of macronutrients and micronutrients, it is unclear whether perchlorate contamination would also be homogeneous.

leachate, according to all labs. A second solid sample contained 2.7 ± 0.3 mg g^{-1}, based on its leachate [value is the average and estimated standard deviation for 10 results (each of which is an average for one of 10 methods)]. It is unclear whether sampling error alone can account for the disparate values. The analytical laboratories were sent the same leachate (one for each solid) and were not working with different portions of the solid. While the AFRL used the data only to assess interlaboratory corroboration of fertilizer analysis by ion chromatography, the results also confirm that there was perchlorate in some of the materials purchased during a specific time period. However, no conclusions should be drawn regarding perchlorate concentrations in specific lots or brands of fertilizer because the inconsistencies in the data were not explored further and the sampling approach was restrictive in nature.

Subsequently, the Water Supply and Water Resources Division of the EPA's National Risk Management Research Laboratory (EPA-ORD-NRMRL-WSWRD) conducted its own survey of fertilizers in a collaboration with the Department of Energy's Oak Ridge National Laboratory (Urbansky, 2000A; Urbansky, 2000D). In addition to a variety of products purchased from home improvement, garden supply or department stores, products were purchased from farming supply stores (e.g., 50-lb bags of urea or ammonium nitrate) in Indiana, Ohio, Kentucky, Pennsylvania, and Tennessee. In addition, commodity chemical samples were collected from local distributors in Ohio and Indiana. These included urea, potassium chloride, ammonium monohydrogen phosphate, and granular triplesuperphosphate, among others. Samples were leached or dissolved and subjected to complexation electrospray ionization mass spectrometry (cESI-MS) or ion chromatography (IC). All IC analyses were performed by the Oak Ridge National Laboratory, which received separate portions of the solid materials. The only products that were found to contain any perchlorate were those based on Chile saltpeter. While this study was the first to include the same products used on production farms, it did not address the issue of sampling.

Sampling strategies for commodity chemicals are always stricky. It is essentially impossible to sample 23,000 tons of urea piled in a warehouse representatively. These products are moved with heavy machinery and transferred to railcars and trucks from barges using conveyor systems and other heavy equipment. It is worth noting that the equipment used for transfer and transportation of these commodities is not normally cleaned thoroughly between uses for different commodities. A common practice is to run a few tons of gravel through the system. Accordingly, traces from residual products are possible.

Fertilizers are normally sampled by taking repeated cores through the piles using a Missouri D tube sampler. The core samples are combined, riffled, divided, and analyzed. These practices are standard within the fertilizer industry and regulatory bodies. Across the nation, state chemists or agriculture departments are obligated to examine fertilizers to verify the manufacturers' reported grades. Sampling practices have evolved to fill those needs. Previous studies generally did not take these practices into account, concentrating instead on the analysis of the solid once a grab sample had been collected. Sampling is of course important to obtain representative results. The distribution of perchlorate is not uniform in Chilean sodium nitrate. For example, in two lots with average concentrations of 1.5 and 1.8 mg g^{-1}, individual 10.0-g grab samples ranged from 0.74 to 1.96 mgg^{-1} (Urbansky, 2001). Information from previous studies and from standard industry practices was used to guide the study reported on in Chapter 2.

Chapter 2
Survey of fertilizers and related materials

2.1. Objectives

In an effort to take into account the difficulties of the matrix, the problems with sampling, and the applicability of the results, this study was undertaken. No single study can say once and for all whether there is perchlorate in fertilizers. However, it is possible to provide a snapshot of current fertilizers commodities. The EPA entered into a collaboration with The Fertilizer Institute, the International Fertilizer Development Center, the Fertilizer Section of the Office of Indiana State Chemist and Seed Commisioner, the North Carolina State University Department of Soil Science (which serves as part of the North Carolina Agricultural Research Service), and IMC-Global for this purpose.

This study was composed of two distinct phases. Phase 1 was designed to evaluate laboratory performance and the ruggedness of the method. Laboratory participation was on a voluntary basis. Laboratories were required to use ion chromatography, but were permitted to choose columns and operating conditions on their own, within certain limits. Phase 1 test samples included a wide variety of fertilizer matrices. In Phase 2, samples of materials were collected from around the nation and sent to the participating laboratories. All data were provided to EPA for evaluation and analysis.

2.2. Phase 1—Evaluation of laboratories

These spanned commodity chemicals, water-soluble plant foods, and granulated/pelletized lawn fertilizers. Phase 1 samples were prepared by EPA-ORD-NRMRL-WSWRD and sent directly to participating laboratories under custody seal. A combination of solid and liquid (aqueous) samples was sent to each laboratory. All of the liquid samples were made by leaching or dissolving the solid in deionized water at a ratio of 10 g dL^{-1} (~10% w/w). All of the raw materials were either American Chemical Society (ACS) reagent grade or demonstrated to be perchlorate-free (within the limits of experimental error) by EPA analyses (Urbansky, 2000A). Cations of the perchlorate salts used to fortify these materials are identified in parentheses. Laboratories were required to demonstrate recovery of fortifications, reproducibility, and ruggedness in real matrices. They were also required to supply experimental details and calibration data. Lastly, quality control specifications were established with regard to number of replicates, blanks, spike recovery, accuracy, and precision. Laboratories were required to estimate limits of detection within each matrix using a standardized procedure. The method has been released as EPA/600/R-01/026, and details covered in the method will not be repeated here.

A set of performance evaluation samples was prepared by EPA-ORD-NRMRL-WSWRD. The identities of these were as follows:

1. agricultural GTSP
2. 1:1 bentonite:kaolinite + 990 μg g^{-1} ClO_4^- (Na^+)
3. agricultural DAP
4. agricultural grade NH_4NO_3 + 620 μg g^{-1} ClO_4^- (Na^+)
5. agricultural grade NH_4NO_3 + 310 μg g^{-1} ClO_4^- (Na^+)
6. duplicate of no. 5
7. ACS reagent urea + 530 μg g^{-1} ClO_4^- (Na^+)
8. ACS reagent urea
9. agricultural KCl (0-0-60)
10. duplicate of no. 9
11. 10 g dL^{-1} aq. ACS reagent urea, K_2SO_4, NaCl, $(NH_4)_2HPO_4$, and KNO_3; xylene cyanole FF
12. duplicate of no. 11
13. no. 11 + 170 μg mL^{-1} ClO_4^- (Na^+ salt)
14. no. 11 + 170 μg mL^{-1} ClO_4^- (NH_4^+ salt)
15. Vigoro lawn winterizer, 22-3-14
16. Scotts lawn winterizer, 22-3-14
17. duplicate of no. 16
18. no. 16 + 1.4 mg g^{-1} ClO_4^-
19. 10 g dL^{-1} (total solids/liquid) aq. agricultural $(NH_4)_2HPO_4$; ACS reagent urea, KCl, $NaNO_3$, $MgSO_4$, bentonite, $CoCl_2 \cdot 6H_2O$, and $NiCl_2 \cdot 6H_2O$
20. no. 19 + 82 μg mL^{-1} ClO_4^- (Na^+ salt)
21. no. 19 + 82 μg mL^{-1} ClO_4^- (K^+ salt)
22. no. 19 + 82 μg mL^{-1} ClO_4^- (NH_4^+ salt)
23. no. 19 + 82 μg mL^{-1} ClO_4^- (NBu_4^+ salt)
24. no. 19 + 82 μg mL^{-1} ClO_4^- ($NOct_4^+$ salt)
25. aq. 6.2 ng mL^{-1} ClO_4^- + FD&C Blue No. 1
26. aq. 34 ng mL^{-1} ClO_4^- in Cincinnati tap water
27. aq. 1.34 μg mL^{-1} ClO_4^- in Cincinnati tap water
28. 10 g dL^{-1} aq. Peter's water soluble plant food, 20-20-20
29. 10 g dL^{-1} aq. Miracle Gro tomato food, 18-18-21
30. 10 g dL^{-1} aq. ACS reagent $(NH_4)_2HPO_4$ + 12 μg mL^{-1} ClO_4^- (Na^+)
31. 10 g dL^{-1} aq. ACS reagent KCl + 74 ng mL^{-1} ClO_4^- (Na^+)

Laboratories were required to demonstrate their ability to detect perchlorate in fertilizers. Some laboratories failed to adequately test

aqueous samples with concentrations in the parts-per-billion, and were cautioned not to dilute samples initially. In Phase 1, the matrix was not identified to the laboratories. This made the process difficult, time-consuming, and resulted in higher errors because it was not possible to initiate corrective measures to handle the needs of a particular matrix. For this reason, major chemical constituents were identified for the laboratories in Phase 2.

The following laboratories successfully completed Phase 1: California Department of Food and Agriculture, Dionex Corporation, American Pacific Corporation (AMPAC), NCSU Department of Soil Science, Montgomery Watson Laboratories (MWL), and IMC-Phosphates Environmental Laboratory.

2.3. Phase 2—Analysis of samples

2.3.1. Sampling and analysis strategy

Phase 2 consisted of the testing of fertilizer samples. The materials sampled represented current major suppliers of production farm fertilizers. Because these were raw materials, they also represented materials used in consumer-oriented fertilizers. Clay additives and other fertilizer products were included, too (e.g., ammonium sulfate). Sampling sites were chosen to reflect national supplies and to provide geographic coverage of raw materials. Samples were procured under the direction of state regulatory agents duly authorized by their agencies and recognized by the Association of American Plant Food Control Officials (AAPFCO) for the collection and examination of fertilizers using accepted procedures.

A number of objectives were established for the choice of samples and the means of collection. Appropriate measures were then taken to achieve these objectives.

1. *To verify the method for analyzing fertilizer materials for perchlorate ion.* To this end, a large number of materials was chosen to represent common matrices and ions that might confound the analytical process. These materials included anions that might interfere with perchlorate determination, e.g., sulfate, chloride, phosphate, and nitrate.

2. *To identify individual sources of contamination if perchlorate ion is found by testing a broad cross section of individual raw materials and nutrient sources throughout the U.S. and include materials from each category (nutrients and fillers) that represent ingredients common to all products.* To this end, we (1) enlisted the help of a large number of material manufacturers and producers; (2) selected products, and consequently materials, from diverse geographic areas; (3) gathered at least three distinct samples of each major nutrient source material, for example, three DAP samples each from different suppliers in diverse geographic locations; (4) identified certain materials as likely candidates for contamination to be sampled without fail, specifically, Chilean nitrate salts, langbeinite ore, and potassium chloride; (5) included at least two samples of leading minor contributor sources such as iron oxide, limestone filler, and clay conditioners that are typically part of fertilizer blends. While many materials have been tested, the list is not exhaustive and was not intended to be. Rather, it focuses on major sources of many chemical commodities used in fertilizer manufacture. Sources of macronutrients and several micronutrients were the principal focus. While some fillers and minor ingredients were tested, the coverage was not comprehensive.

   Raw materials rather than finished products were focused on for two reasons: (1) If perchlorate were present in blended fertilizers, it would have had to come from a specific raw material in the blend (assuming it was not intentionally added); finished product sampling would not identify a specific contaminant. (2) Raw materials should contain higher concentrations than formulated products (i.e., blending dilutes the analyte) and their analyses are likely to suffer fewer matrix effects. Products are listed in Table 2.1.

3. *To ensure correct sampling and third party validation, and to maintain a chain of custody throughout the sampling, transport, preparation, and distribution process.* To this end, samples were taken under the supervision of state officials authorized by state statutes to collect samples of fertilizers, such as state chemists or agriculture department officers. In addition to manuals from The Fertilizer Institute (TFI), Association of Official Analytical Chemists (AOAC, 2000a, 2000b), and the AAPFCO (1999), written instructions were issued to each inspector outlining the specific protocol to be used. These instructions were in addition to and complementary to the standard sampling practices. In a few cases, state inspectors were unavailable, and knowledgeable practioners from industry were permitted to collect the sample; this has been noted in Table 2.1. Sampling was conducted at the actual production site whenever possible to eliminate potential for contamination by other materials. The collected samples were sent under custody seal to the International Fertilizer Development Center (IFDC) for riffling, grinding, and packaging. The IFDC sent the custody-sealed packages to the participating laboratories.

4. *To obtain consensus from governmental, industrial, and academic interests on how to accomplish these goals.* All documents and proposals were reviewed by TFI, IMC-Agrico, EPA-ORD-NERL-ERD, EPA-ORD-NRMRL-WSWRD, NCSU Department of Soil Science, Office of Indiana State Chemist (OISC) Fertilizer Section, U.S. Air Force Research Laboratories, and the AOAC Fertilizer Referee.

A series of quality control samples were prepared for Phase 2 by EPA-ORD-NRMRL-WSWRD and sent to the IFDC for distribution to the participating laboratories. Each laboratory submitted its results to EPA-ORD-NRMRL-WSWRD for evaluation and tabulation. Laboratories were required to submit chromatograms for the sample solutions and fortifications they made to demonstrate acceptable recovery in the matrix. Laboratories were also required to submit proof of the goodness of their calibrations, instrument performance, detection limit, and sensitivity.

2.3.2. Results

Table 2.2 shows the results obtained by the laboratories that elected to participate in Phase 2. All of the samples were tested by NCSU, CDFA, IMC, and AMPAC; not all of the samples were tested by Dionex. Positive hits above the assured reporting level (ARL) were rechecked. The calculation of the assured reporting level is described in detail in the method itself, EPA/600/R-01/026 (Collette, 2000).

Other than nonzero results reported by one lab, perchlorate was detectable only in materials derived from Chilean caliche. It must be emphasized that these nonzero results were still below the ARL except for item 48. In the case of item 48, a granular triplesuperphosphate, the same lab obtained discrepant results of 26 $\mu g g^{-1}$ (with an ARL of 20 $\mu g g^{-1}$) and undetectable (with an ARL of 100 $\mu g g^{-1}$). Given that no other laboratory obtained similar results, this suggests that the 26 $\mu g g^{-1}$ value is erroneous, and it has been rejected as an outlier. Initially, this lab found 44.5 $\mu g g^{-1}$ in item 23, an ammonium dihydrogen phosphate (MAP). However, it reported that perchlorate was undetectable when requested to reanalyze the material. In addition, a portion of an archived sample of item 23 was sent to this lab by EPA-ORD-NRMRL-WSWRD for analysis; this portion also failed to show detectable perchlorate. Consequently, the original value was discarded as faulty.

Samples of materials 5, 23, 40, and 42 were analyzed independently by MWL and by EPA-ORD-NERL-ERD. MWL found 2675 $\mu g g^{-1}$ in item 42, while NERL found 2845 $\mu g g^{-1}$. These values are consistent with results reported by other laboratories. Perchlorate was undetectable in 5, 23, and 40, according to both MWL and EPA-ORD-NERL-ERD.

Recoveries of fortifications ranged from 81% to 111%, regardless of the specific increase in concentration resulting from spiking. The increases in concentration, $\Delta[ClO_4^-]$, and the recoveries are reported in Table 2.3. All laboratories demonstrated satisfactory performance in this regard. Although not explicitly reported here, the ARLs can be computed from the information in Table 2.3.

2.3.3. Discussion

It is worth pointing out at the U.S. Geological Survey and Air Force Research Laboratories have found perchlorate in isolated samples of sylvite taken from New Mexico (Harvey, 1999). USGS is engaged in additional sampling of North American mining sites in order to assess whether there are natural mineral deposits of potassium perchlorate in sylvite or sylvinite. Because little is known about the mechanisms of perchlorate formation in the natural environment (which are assumed to be meteorological in nature), it is not clear whether these findings represent a low-level background to be expected in evaporite mineral deposits or not. There is, of course, the possibility for anthropogenic perchlorate formation to occur during blasting operations to mine potassium chloride, but it has not been observed. Nonetheless, perchlorate has not been detected in any samples of agricultural grade potassium chloride (0-0-62 or 0-0-60) taken under the auspices of the EPA (items 4, 8, and 28). Nor was it found in a langbeinite sample (item 13), acquired via blasting. Current data are inadequate to demonstrate that KCl or $K_2Mg_2(SO_4)_3$ suffer from inclusions of perchlorate salts to an environmentally relevant extent.

Previous EPA-ORD-NERL-ERD and AFRL findings cannot be applied to fertilizers as a whole because of the composition and nature of the products investigated. Those findings may have reflected a temporal contamination of one or more raw materials or an error in manufacture. The only fertilizers unequivocally and consistently demonstrated to contain perchlorate were bagged products deriving some or all of their nitrogen from Chilean nitrate salts, which are known to vary in perchlorate content. Even though perchlorate was previously identified in some fertilizer products and was presumably introduced through a contaminated raw material, this incident appears to have been isolated and the source of the perchlorate remains an enigma, for some of these products had no known link to Chile saltpeter. Furthermore, awareness within the fertilizer industry and the environmental community is now substantially heightened.

Based on the studies thus far (Collette, 2000; Gu, 2000; Urbansky, 2000A; Urbansky, 2000D; Urbansky, 2000E; Robarge, 2000), there is a consensus among researchers that there is insufficient evidence for fertilizers to be viewed as contributors to environmental perchlorate contamination, except for imported Chile saltpeter or products derived from it. The potential future influence of such products is further reduced by SQM's modified refining process to lower perchlorate concentration in its products. Within the limits of experimental error and current ion chromatographic technology, agricultural products tested by EPA-ORD-NERL-ERD, ORNL, and EPA-ORD-NRMRL-WSWRD all were devoid of perchlorate as were all of the products in this survey except for those known to contain or to be derived from mined Chile saltpeter. While the results presented herein reflect another such snapshot, it is the most comprehensive examination of fertilizers and related materials to date. As with any environmental contaminant, an individual study is limited in applicability to the future. Nonetheless, the weight of evidence obtained to date largely argues against fertilizers as sources of environmental perchlorate. That notwithstanding, it would not be imprudent for manufacturers, trade associations, or the industry to establish periodic monitoring practices to screen either raw materials or finished products for perchlorate in a manner similar to how finished drinking water is tested, perhaps with some allowance for periodic phenomena.

Table 2.1. Fertilizers and related materials surveyed for perchlorate

Item	Composition	Manufacturer/supplier	Authority of
1	Lawn fertilizer, 22-3-14	Scotts Company, Marysville, OH	ODA
2	Ammonium monohydrogen phosphate (DAP)	IMC-Agrico	ODA
3	Urea	Potash Corporation of Saskatchewan	ODA
4	Potassium chloride (MOP)	Potash Corporation of Saskatchewan	ODA
5	Iron oxide	Sims Agriculture	ODA
6	Limestone	Millersville Lime	ODA
7	Potassium magnesium sulfate (Sul-Po-Mag)	IMC-Kalium, Carlsbad, NM	CDFA§
8	Potassium chloride (MOP)	Mississippi Potash, Carlsbad, NM	CDFA§
9	Osmocote 18-6-12	Scotts, Marysville, OH	ODA
10	Miracle Gro lawn fertilizer, 36-6-6	Scotts, Port Washington, NY	ODA
11	Miracle Gro plant food, 20-20-20	Scotts, Port Washington, NY	ODA
12	Langbeinite, mechanical mining	IMC-Kalium, Carlsbad, NM	NMDA
13	Langbeinite, drill and blast	IMC-Kalium, Carlsbad, NM	NMDA
14	Potassium magnesium sulfate (Sul-Po-Mag)	IMC-Kalium, Carlsbad, NM	NMDA
15	Limestone	Chemical Lime, Salinas, CA	CDFA§
16	Ammonium sulfate	Simplot, Pocatello, ID	CDFA§
17	Urea	Unocal†	CDFA§
18	Ammonium sulfate	Dakota Gasification, Bismarck, ND	CDFA§
19	Ammonium monohydrogen phosphate (DAP)	IMC-Agrico	FDACS‡
20	Potassium magnesium sulfate (Sul-Po-Mag)	IMC-Kalium	FDACS‡
21	Potassium sulfate	IMC-Kalium	FDACS‡
22	Ammonium sulfate	Dutch State Mines (DSM)	FDACS‡
23	Ammonium dihydrogen phosphate (MAP)	IMC-Agrico	FDACS‡
24	Iron oxide	Fritt Industries, Ozark, AL	FDACS‡
25	Limestone	E.R. Jahna, Lake Wales, FL	FDACS‡
26	Urea	Unocal†	FDACS‡
27	Clay	Ag Sorb	FDACS‡
28	Potassium chloride	PCS	FDACS‡
29	Urea	CF Industries, Donaldsonville, LA	supplier
30	Ammonium nitrate	LaRoche, Atlanta, GA	IFDC□

Table 2.1 continued

Item	Composition	Manufacturer/Supplier	Authority of
31	Ammonium monohydrogen phosphate (DAP)	Agrium, Soda Springs, ID	
32	Ammonium dihydrogen phosphate (MAP)	Agrium, Soda Springs, ID	
33	Potassium sodium nitrate	SQM	FDACS⊗
34	Ammonium nitrate	Mississippi Chemical, Yazoo City, MS	FDACS⊗
35	Potassium nitrate	SQM	FDACS⊗
36	Sodium nitrate	SQM	FDACS⊗
37	Ammonium nitrate	Mississippi Chemical, Yazoo City, MS	FDACS⊗
38	Granular triplesuperphosphate	Cargill, Riverview, FL	
39	Ammonium dihydrogen phosphate (MAP)	Simplot, Pocatello, ID	
40	Ammonium monohydrogen phosphate (DAP)	Simplot, Pocatello, ID	
41	Limestone	Georgia Marble	
42	Potassium nitrate	SQM	
43	Plant food, 10-10-10	SSC, Statesville, NC	supplier
44	Clay	Oil Dry Co., Ripley, MS	Pursell Ind.¶
45	Potassium magnesium sulfate	IMC-Kalium, Carlsbad, NM	Pursell Ind.¶
46	Potassium nitrate	Vicksburg Chemical Co., Vicksburg, MS	manufacturer
47	Ammonium monohydrogen phosphate (DAP)	PCS, Aurora, NC	manufacturer
48	Granular triplesuperphosphate	IMC-Agrico, Mulberry, FL	manufacturer
Quality control samples prepared by EPA-ORD-NRMRL-WSWRD (all solids)			
49	Potassium chloride + 6.8 mg $ClO_4^- g^{-1}$	J.T. Baker (Phillipsburg, NJ) ACS reagent KCl and $KClO_4$	EPA
50	Peter's water soluble plant food, 20-20-20 + 6.2 mg $ClO_4^- g^{-1}$	Scotts (Marysville, OH) + GFS (Columbus, OH) ACS reagent $NaClO_4$	EPA
51	Granular triple superphosphate + 2.7 mg $ClO_4^- g^{-1}$	A.H. Hoffman (Lancaster, PA) + GFS ACS reagent $NaClO_4$	EPA
52	Urea + 1.8 mg $ClO_4^- g^{-1}$	D.W. Dickey & Son (Lisbon, OH) + Aldrich (Milwaukee, WI) ACS reagent NH_4ClO_4	EPA
53	Potassium chloride (no analyte added)	CF Industries (Cincinnati, OH) + A.H. Hoffman	EPA
54	Ammonium nitrate (no analyte added)	Cargill (Shelbyville, KY)	EPA
55	Chilean sodium nitrate (Chile saltpeter)○	A.H. Hoffman (mfd. by SQM)	EPA

Key: Fertilizers: Sul-Po-Mag = sulfate of potash/magnesia, MOP = muriate of potash, DAP = diammonium phosphate, MAP = monoammonium phosphate. Manufacturers/suppliers: PCS = Potash Corporation of Saskatchewan; SQM = Sociedad Quimíca y Minera. Authorities: CDFA = California Department of Food and Agriculture; FDACS = Florida Department of Agriculture and Consumer Services; NMDA = New Mexico Department of Agriculture; ODA = Ohio Department of Agriculture. †Unocal is now owned by Agrium. ‡Sampled at Pursell Industries in Winterhaven, Florida. ⊗Sampled at Gro-Mor Co., Inc., Plant City, FL. §Sampled at Pursell Industries, Los Angeles, California. ¶Pursell Ind. = Pursell Industries, a supplier for the manufacturers listed (located in Orrville, Ohio). □Material was purchased by IFDC for this study. ○This material had previously been found to contain 1.7 mg $ClO_4^- g^{-1}$ by EPA-ORD-NRMRL-WSWRD; no perchlorate salts were added to increase this value.

Table 2.2. Summary results for perchlorate concentration detected by replicate analyses of samples listed in Table 2.1¶

Item	Calif. Dept. of Food & Agric.		NCSU Dept. of Soil Science		American Pacific Corporation		IMC Environ. Laboratory		Dionex Corporation	
	$[ClO_4^-]$ $\mu g\ g^{-1}$	diln† 1 to	$[ClO_4^-]$ $\mu g\ g^{-1}$	diln 1 to	$[ClO_4^-]$ $\mu g\ g^{-1}$	diln 1 to	$[ClO_4^-]$ $\mu g\ g^{-1}$	diln 1 to	$[ClO_4^-]$ $\mu g\ g^{-1}$	diln 1 to
1	u§	100	u	100	0.3*	10	u	10		
2	u	50	u	500	u	100	u	100	u	100
3	u	25	u	100	2*	50	u	50		
4	u	50	u	100	0.3*	10	u	100	u	100
5	u	10	u	100	0.6*	10	u	10		
6	u	5	u	100	u	1	u	100		
7	u	500	u	100	u	10	u	100	u	100
8	u	10	u	100	u	10	u	10	u	100
9	u	100	u	500	u	100	u	100	u	100
10	u	50	u	500	u	1000	u	10	u	100
11	u	500	u	500	u	100	u	100		
12	u	50	u	100	u	10	u	100		
13	u	50	u	100	u	50	u	10		
14	u	50	u	100	u	50	u	10		
15	u	5	u	100	u	5	u	10	u	100
16	u	25	u	100	u	50	u	50	u	100
17	u	25	u	100	u	2	u	10		
18	u	25	u	100	u	50	u	100		
19	u	100	u	500	u	10000	u	50	u	100
20	u	500	u	100	u	10	u	100		
21	u	50	u	100	u	50	u	100		
22	u	10	u	100	1.5*	50	u	10		
23	u	200	u	500	u	50	u	100	u	100
24	u	10	u	100	1	10	u	100		
25	u	5	u	100	u	1	u	10		
26	u	25	u	100	0.4*	10	u	100		
27	u	2	u	100	1.5*	50	u	10		
28	u	25	u	100	0.3*	10	u	100		
29	u	25	u	100	0.4*	10	u	50	u	100
30	u	5	u	100	u	20	u	10		

Table 2.2 continued

Item	Calif. Dept. of Food & Agric.		NCSU Dept. of Soil Science		American Pacific Corporation		IMC Environ. Laboratory		Dionex Corporation	
	$[ClO_4^-]$ µg g^{-1}	diln† 1 to	$[ClO_4^-]$ µg g^{-1}	diln 1 to	$[ClO_4^-]$ µg g^{-1}	diln 1 to	$[ClO_4^-]$ µg g^{-1}	diln 1 to	$[ClO_4^-]$ µg g^{-1}	diln 1 to
31	u	100	u	500	u	500	u	100		
31d‡	u	500	u	500	u	50	u	100		
32	u	250	u	500	u	1000	u	100	u	100
33	3700	4000	4020	5000	4200	10000	4066	5000	3860	5000
33d	3925	5000	4270	5000	3700	10000	4136	5000	3850	5000
34	u	5	u	50	0.9*	10	u	100		
34d	u	5	u	10	u	50	u	10	u	100
35	2624	4000	2380	2000	2100	5000	2288	2000	2240	2000
36	1860	2000	1950	2000	1800	5000	2054	2000	1920	2000
37	u	5	u	100	u	10	u	10		
38	u	1000	u	500	u	1000	u	50	u	1000
39	u	500	u	500	u	100	u	1000		
40	u	200	u	500	2.5*	50	u	100	u	1000
41	u	5	u	100	u	1	u	10	u	100
42	2424	4000	2542	2000	2050	5000	2455	2000	2340	2000
43	u	100	u	100	u	100	u	10		
44	u	2	u	100	0.3*	10	u	10		
45	u	50	u	100	u	50	u	50		
46	u	25	u	100	u	5	u	50		
47	u	250	u	500	u	100	u	10	u	100
48	u	1000	u	500	26**	100	u	100	u	1000
48d	u	500	u	500	u**	1000	u	100	u	1000
49	5720	10000	5960	5000	6200	10000	6377	5000	6140	10000
50	5730	5000	5190	5000	5100	10000	5737	5000	5430	10000
51	2540	4000	2700	2000	2080	2000	2376	2000	2300	10000
52	1540	2000	1790	2000	1430	1000	1511	1000	1810	10000
53	u	10	u	100	0.5	10	u	10		
54	u	5	u	100	u	10	u	10		
55	1550	2000	1580	2000	1440	1000	1680	1000	1700	2000

¶Sample loops were 1000 µL exceptfor Dionex, which used 500 µL. †Dilution factor refers to subsequent dilution of a stock solution prepared by leaching or dissolving the material at 10 g dL^{-1} (~10% w/w).‡Samples 31, 33, 34, and 48 were supplied to the laboratories as blind duplicates. §The designation "u" means undetected, i.e., no peak could be distinguished from the baseline. *Values falls below the assured reporting level and therefore cannot be viewed as meaningful; see the method (EPA/600/R-01/026) for details on how the ARL is determined. **See text for explanation.

Table 2.3. Tested fortifications (spikes) and recoveries in solutions of samples listed in Tables 2.1–2.2

Item	Calif. Dept. of Food & Agric.		NCSU Dept. of Soil Science		American Pacific Corporation		IMC Environ. Laboratory		Dionex Corporation	
	$\Delta[ClO_4^-]$ $\mu g\ g^{-1}$	recov %	$\Delta[ClO_4^-]$ $\mu g\ g^{-1}$	recov %	$\Delta[ClO_4^-]$ $\mu g\ g^{-1}$	recov %	$\Delta[ClO_4^-]$ $\mu g\ g^{-1}$	recov %	$\Delta[ClO_4^-]$ $\mu g\ g^{-1}$	recov %
1	10	98	10	101	10	93	200	85		
2	10	102	50	98	10	90	200	100	10	107
3	10	107	50	93	10	103	200	102		
4	10	109.5	10	93	10	97	200	98	10	103
5	10	98	10	87	10	97	200	89		
6	10	104	10	98	10	93	200	100		
7	10	93	50	85	10	106	200	103	10	96
8	10	108	30	96.5	10	93	200	87.5	10	101
9	10	104	50	101	10	103	200	96.5	10	98
10	10	99	50	101	10	93	200	97	10	96.5
11	10	101	50	95	10	109	200	99		
12	10	100	10	88	10	91	200	104		
13	10	92	50	89	10	92	200	80.5		
14	10	96	50	88	20	90	200	88		
15	10	105	10	96	10	91	200	117	10	108
16	10	106	50	86.5	10	95	200	99	10	106
17	10	90	10	96	10	108	200	93		
18	10	106	50	94	10	97	200	97.5		
19	10	93	50	97	10	107	200	97	10	110
20	10	101	50	88	10	106	200	102		
21	10	95	50	91	10	96	200	103		
22	10	107	50	81.5	10	95	200	85		
23	10	98	50	99	50	92	200	95	10	106
24	10	107	10	84	10	106	200	103		
25	10	97	10	96	10	99	200	93		
26	10	96	10	97	10	106	200	102.5		
27	10	92	10	92	10	93	200	107		
28	10	102	30	94	10	94	200	98.5		
29	10	105	10	95	10	91	200	105	10	110
30	10	100	10	95	10	101	57	96.5		

Table 2.3 continued

Item	Calif. Dept. of Food & Agric.		NCSU Dept. of Soil Science		American Pacific Corporation		IMC Environ. Laboratory		Dionex Corporation	
	$\Delta[ClO_4^-]$ µg g^{-1}	recov %	$\Delta[ClO_4^-]$ µg g^{-1}	recov %	$\Delta[ClO_4^-]$ µg g^{-1}	recov %	$\Delta[ClO_4^-]$ µg g^{-1}	recov %	$\Delta[ClO_4^-]$ µg g^{-1}	recov %
31	10	100	50	95	10	91	200	98		
31d‡	10	95	50	97	10	94	200	98		
32	10	97	50	97	10	93	400	98	10	103
33	50	90	100	100	20	95	57	98	100	102
33d	50	102	50	107.5	20	103	57	97	100	101
34	10	100	50	81	20	106	57	93.5		
34d	10	102	10	97	10	102	200	85	10	102
35	10	109	100	98	30	104	57	98.5	100	106
36	10	107	100	98	20	105	57	98	100	103
37	10	94	10	99	10	102	57	91		
38	10	95	50	108	10	100	200	88	10	98
39	10	101	50	95	10	92	200	103		
40	10	94	50	98	10	93	200	101	10	110
41	10	93	10	98	10	103	200	97	10	99
42	50	108	100	99	30	98	57	97	100	105
43	10	96	50	93	10	109	200	88.5		
44	10	94	10	91	10	93	200	88.5		
45	10	91	10	91	10	102	200	109		
46	8	104	10	94.5	10	105	200	101		
47	10	103	50	99	10	92	200	81	10	100
48	10	110	50	99	20	102	200	91	10	96
48d	10	92.5	50	105	10	103	200	94	10	105
49	50	104	100	97	50	95	20	101	50	95
50	40	95	100	109	50	93	57	95	40	99
51	100	93	100	111	60	105	20	98	20	105
52	50	105	100	97.5	50	91	20	100	20	102
53	10	102	10	92.5	10	91	200	94		
54	10	101	10	100	10	109	200	110		
55	50	103	100	100	50	94	57	96	100	102

Chapter 3
Implications for vascular plants

3.1. Introduction

In the laboratory setting, some plant species will absorb perchlorate when exposed to perchlorate via irrigation water. This has been explored for possible phytoremediation (Nzengung, 1999; 2000). Some investigators have speculated that bacteria are responsible for perchlorate reduction in plants. Perchlorate-reducing monera have been identified by several laboratories, and cultured from a variety of sources (including Las Vegas Wash sediments, food processing sludge, and sewage sludge) (Logan, 1998; Coates, 1999; Coates, 2000). This suggests that perchlorate-reducing bacteria are active in the environment. On the other hand, the bacteria isolated thus far prefer oxygen over nitrate over perchlorate. In order for perchlorate reduction to occur, the water must be anoxic, and all of the nitrate must have been consumed. Moreover, these bacterial cultures require a suitably moist environment. Arid soils or regions with low rainfall may not sustain their growth. Natural attenuation probably varies around the nation, depending on local factors; therefore, it is not possible to draw any conclusions about the ecological impact of using fertilizers that contain perchlorate, for they may be applied in areas where bacterial degradation occurs.

Due to the reported occurrence of perchlorate in certain water resources and in certain fertilizer products, several groups have begun to address the extent and significance of perchlorate uptake by plants. For example, if produce is grown using perchlorate-tainted irrigation water or fertilizers and the perchlorate is retained in the edible portions, this might constitute a route of human exposure. The possibility of exposure would be further increased if perchlorate were shown to survive various types of processing. Unfortunately, experimental results that definitively gauge the extent of risk from this route of exposure have not yet been published. However, some significant progress toward this goal has been made. Work is ongoing in this area, and several projects are proceeding at the Institute of Environmental and Human Health of Texas Tech University.

3.2. Complicating factors

One problem with uptake studies is the possibility of convolved influences on uptake. There are perchlorate absorption data available for only a few species of vascular plants. The absorption and accumulation of anionic solutes can be affected by many physical and chemical properties, such as concentration, size, charge density, and aquation.

3.2.1. Chemical influences on ion transport

Ion transport through plasma membranes occurs via transport proteins (Raven, 1999). At present, there are no published reports on the transmembrane transport of perchlorate in plants at the molecular or cellular level. In the absence of studies specifically examining influences on transmembrane perchlorate transport, it is necessary to consider whether previously published or ongoing uptake studies have accounted for likely influences.

Pertechnetate (TcO_4^-) is similar in size (ionic radius) and Gibbs free energy of aquation (Moyer, 1997). In aerobic aquatic environments, pertechnetate is highly mobile, accumulated by plants, and not appreciably retained by many soils (Sheppard, 1991); therefore, it is like perchlorate in many respects. One respect in which it differs is its ease of reduction to an immobile species, TcO_2 (Tagami, 1996). Unlike perchlorate, many papers have been published on the fate and transport of pertechnetate in food plants due to its release after use in medical imaging or from nuclear installations. Given the similarities between ClO_4^- and TcO_4^-, those factors that influence pertechnetate uptake should be either accounted for or ruled out in perchlorate uptake studies. Depending on the plant, pertechnetate absorption and accumulation can be affected by nitrate (Kriger, 2000; Echevarria, 1996; 1998), sulfate (Cataldo, 1978; 1983), and phosphate (Cataldo, 1978; 1983; Echevarria, 1996; 1998). No studies on perchlorate uptake have attempted to account for the impacts of other ionic species.

3.2.2 Concentration

Active transport of perchlorate has not been reported. However, both active and passive transport of an ion are affected by its concentration (Raven, 1999). All ions experience an electrochemical gradient which is determined in part by the ion's concentration. Past and ongoing studies have exposed plants to much higher concentrations than are present in the environment.

For example, Hutchinson and coworkers are presently studying greenhouse-grown lettuce irrigated with perchlorate-tainted water. Lettuce is of particular importance for assessing the risk of perchlorate to the food supply since much of the lettuce produced in the U.S. is irrigated with perchlorate-tainted water. Also, lettuce has a high water content and virtually the entire aboveground plant is consumed without cooking or processing. Lettuce plants are watered with one of five different concentrations of perchlorate (0.1, 0.5, 1.0, 5.0, and 10.0 $\mu g\ mL^{-1}$) for a period of 90 days following planting. At various intervals

of time, whole plants were harvested and divided into green tissue and root samples; each sample was analyzed for perchlorate. The analytical method was adapted from Ellington and Evans (2000). Levels of perchlorate rise steadily over the first 50–60 days, and then generally level off. The amount of perchlorate detected in the leaves correlates with dose. As an example, at about 50 days into the experiment, the lettuce irrigated with 10.0 $\mu g\ mL^{-1}$ perchlorate exhibits a perchlorate content of about 3 $mg g^{-1}$ on a lettuce dry matter basis. Since lettuce is about 90% water, this would amount to about 0.30 $mg\ g^{-1}$ on a wet mass basis. Experiments are underway to determine whether lettuce has the capability to degrade perchlorate if the supply of the contaminant is stopped; however, initial data suggest that increases in biomass are responsible for the apparent reduction in perchlorate content. Therefore, a decline in concentration (e.g., expressed as $mg g^{-1}$) does not adequately reflect the situation. While the preliminary results from these studies (Hutchinson, 2000) represent progress in understanding perchlorate in consumable produce, it must remembered that the perchlorate concentrations are about 500 times the concentrations in perchlorate-tainted irrigation water and that results obtained under laboratory growing conditions cannot be directly extrapolated to edible agricultural produce.

3.2.3. Tissue-specific accumulation

All studies of perchlorate occurrence in plants have focused on the leaves, stalks, and wood. While the leaves of some plants (e.g., lettuce) are consumed, the leaves of many others are not. Other than lettuce, no studies have been conducted on absorption and accumulation in edible fruits and vegetables. Therefore, information on uptake by *Tamarix ramosissima* (Urbansky, 2000C), *Salix* (Nzengung, 1999; 2000) tobacco (Wolfe, 1999) and *Myriophyllum aquaticum* (Susarla, 1999B; 1999C) cannot be directly applied or extrapolated to food crops. While many ions are transported via the xylem, the phloem supplies many of the nutrients to fruit. Although dissolved salts are carried into the xylem along with the water, the phloem relies on active transport. Because the edible portions of many plants (e.g., tubers, roots, some fruits) experience little to no transpiration, the phloem—rather than the xylem—carries both inorganic and organic materials for nutrition (Salisbury, 1992). For example, nitrate is almost never present in phloem (Salisbury, 1992), and is rarely found in fruit.

It is worth pointing out that studies on pertechnetate uptake showed that this anion was selectively accumulated in specific parts of plants and generally not in the consumable tissues. Cataldo (1986), Echevarria (1997), and Gast (1978) demonstrated that a variety of food plants could absorb and accumulate pertechnetate, with most of the ion in the roots or leaves rather than edible portions. While TcO_4^- was shown to enter tomato leaf tissue via the xylem (Krijger, 1999), the fruit—which is actually consumed—was never tested. Accordingly, these observations demonstrate the importance of sampling consumable plant tissues and not just foliage. Furthermore, they warn against drawing inferences about fruit (or other edible portions) based on occurrence in foliage.

3.2.4. Soil sorption

It is generally accepted that perchlorate adsorbs to soil particles through outer-sphere complexes where the ions engage in simple electrovalent bonds and serve to balance electric charge on the surface (Sparks, 1995; Sposito, 1989). Such adsorption is often influenced by pH due to protonation of mineral oxo moieties, as is the case with goethite (Gurol, 2000; Sasaki, 1983) or γ-Al_2O_3 (Sasaki, 1983). Similar outer-sphere behavior has been observed by others as well, especially when perchlorate salts have been used to vary ionic strength and to provide a competitor to probe adsorption of another anion (Bourg, 1978; Gisler, 1980; Hundal, 1994; Ji, 1992; Kummert, 1980; Rhue, 1990; Sadusky, 1991; Sigg, 1981; Zachara, 1988; Zhang, 1996). The number of available binding/exchange sites is finite, but very large, permitting soil to act as a reservoir for anions. Outer-sphere complex formation is reversible and generally labile, but the sheer number of active sites can lead to a buffering effect on aqueous ion concentration, especially if the soil is far from saturated with the ion. This phenomenon is further affected by ionic strength. Under high ionic strength conditions (i.e., large concentrations of soluble and dissociable salts), less adsorption is possible for any one particular ion. In the case of diffuse ion swarms, where aquated counterions (anions in this case) hover near the surface in an ion-pair like situation, association with the positively charged surface is fleeting and constantly changing, with no real effect on availability of the ion to the aqueous phase.

Even though soil scientists routinely use perchlorate salts as indifferent electrolytes, it is possible that some soil types could resist desorption. In addition, sorption phenomena in soil are often more complicated than those in simpler (e.g., aqueous) chemical systems. Despite the principle of microscopic reversibility, which requires that the same pathway for adsorption be available for desorption, the thermodynamics of the sorption equilibrium affect the activation energy of the desorption process. Consequently, it is not unusual for desorption to occur via a different mechanism than the simple reverse of the one for adsorption (Sparks, 1995). Sorption phenomena have not been accounted for in any of the adsorption-accumulation studies conducted thus far. Transport of ions through soil is also a complex process (Jury, 1992; Goldberg, 1992; Selim, 1992). It can be difficult to account for in the laboratory setting due to the additional impacts of hydrologic, meteorologic, and geomorphologic factors, which are location-dependent. Moreover, ion exchange is often transport-controlled (Sposito, 1994).

3.2.5. Summary

To be applicable, studies of perchlorate absorption and accumulation must control for a variety of complicating factors. The presence of other anions either from co-administration in fertilizers or background salts present in the water supply may suppress uptake. Interspecies variation in absorption mechanisms may lead to differing levels of absorption and differing locations of accumulation. It is important to know if accumulation occurs in fruits versus in leaves or as a result of foliar application versus root application (as in irrigation). The rate of harvesting may lead to different rates of uptake by disrupting normal physiological processes in the plants. Lastly, the effect of soil (primarily sorptive in nature) must be considered. Careful agronomic studies are required to account for such influences, which are likely to complicate studies on the impact of contaminated irrigation water, too.

3.3. Difficulties in analysis

Another problem that has delayed accurate and definitive studies of perchlorate uptake by edible plants is the difficulty of analyzing for perchlorate in plant materials. Ion chromatography is currently the recommended method for routine analysis of inorganic ions such as perchlorate. It is a sensitive, reliable, and easily-implemented technique when perchlorate occurs in a matrix that has a relatively low level of total dissolved solids (TDS). Unfortunately, in a matrix with high TDS (which largely equates to high ionic strength), other ions can swamp the conductivity detector and effectively mask the signal from perchlorate. This has proven to be a very difficult problem with extracts of plant materials, many of which exhibit high TDS. In addition to potentially high levels of other inorganic ions, extracts of plant materials typically contain amino acids, other carboxylates or carboxylic acids (e.g., citrate, ascorbate, fatty acids) sugars, and nucleotides; all of which contribute to the ionic environment of the sample (Ellington, 2000). Ion chromatography is not alone in this regard. Other techniques and methods suitable for reasonably dilute drinking water matrices (Urbansky, 2000C; Magnuson, 2000A; Magnuson, 2000B) cannot be readily applied to fertilizers or botanical and physiological fluids. The problems of trace ionic analysis have led to development of other methods that rely on instrumentation that is common in high-end research laboratories, such as asymmetric waveform ion mobility mass spectrometry (Handy, 2000; Ells, 2000) or tandem MS-MS systems (Koester, 2000). Another option used for eliminating dissolved matter is selective preconcentration of the perchlorate on an anion-exchange resin (personal communication from Baohua Gu).

Recently, Ellington and Evans (2000) have reported an IC-based method for the analysis of perchlorate in plant materials, which greatly reduces interferences from high TDS. Their method involves first freeze-drying the plant material and then grinding it through a 30-mesh screen. The ground material is then mixed with water and heated for 0.5 hours in a boiling water bath in order to saturate the dry material and to precipitate proteins. The saturated samples are then shaken and stored at 3°C overnight. Next, the samples are centrifuged and the supernatant is filtered. With most plant materials, this produces a very highly colored solution that contains numerous inorganic and organic ions. Prior to analysis, Ellington and Evans add these highly colored extracts to alumina sorbent (DD-6) and allow them to stand for 20 hours at 3 °C. Finally, the extracts are filtered through an activated cartridge that contains divinylbenzene. The highly colored extracts are rendered colorless, and the ionic level is reduced dramatically. The minimum reporting level (MRL) of perchlorate in lettuce and tomato was found to be approximately 250 $\mu g\ g^{-1}$ on a wet mass basis.

Lettuce and tomato were chosen as representative plants because they are considered high priority candidates for screening studies of perchlorate in foodstuffs (Ellington, 2000) However, it should be noted that in this work, native perchlorate was not detected in any produce, nor was the method applied to any edible plants that were grown with intentional exposure to perchlorate. Instead, perchlorate was spiked into the extraction water for one half of the duplicate freeze-dried samples, while one half were extracted with pure water; consequently, sorptive loss to plant tissue is not entirely precluded. Ellington and Evans (2000) were able to evaluate the efficacy of the clean-up procedure for lettuce and tomato in light of the impact on the known perchlorate concentration in the spiked extracts. They observed no loss of perchlorate in spite of the efficient removal of other inorganic (and also organic) ions. This is tentatively attributed to preferential and competitive adsorption on the alumina. This assertion is supported by the observation that 40% of perchlorate is lost from solution when exposed to alumina in the absence of other ions. However, loss of perchlorate is not expected when the method is applied to plant material because most extracts have high levels of TDS. Despite some remaining uncertainties, the method of Ellington and Evans (2000) advances the assessment of potential risk posed by eating produce grown in the presence of perchlorate-tainted irrigation water or fertilizer.

3.4. Implications of perchlorate absorption and accumulation

An obvious concern raised by finding measurable perchlorate concentrations in plant tissues is whether this ion can affect food crops. Most domestic crops are fertilized using commodity chemicals with no known link to perchlorate contamination. Some crops (e.g., corn, wheat, and rice) are fertilized with nitrogen fertilizers that should be perchlorate-free because of the manufacturing processes. There is no reason to suspect any perchlorate associated with growing grains.

The only crops with documented use of Chilean nitrate products are tobacco and citrus fruits. Data on application of perchlorate-containing fertilizers is sparse or nonexistent, and it is not possible to estimate the ecological impact in any meaningful way. Modest information is available on uptake by tobacco, but this is not a food crop, and the use of Chilean nitrate salts appears to be locale-dependent.

Depending on the season, sources of fresh and processed fruits and vegetables vary considerably between domestic and imported. EPA has no data regarding the reliance on perchlorate-containing fertilizers for food crops grown outside the U.S. It is not known whether fruits or vegetables absorb and retain perchlorate ion under typical growing conditions (Cf. §3.2); accordingly, it is not possible to say whether produce can serve as an exposure route at this time. There are no published data on perchlorate in imported produce, no published data on perchlorate in domestic produce, and minimal data from controlled laboratory or field experiments on absorption and accumulation in food crops; therefore, it is impossible to assess whether foodstuffs contribute to perchlorate consumption in humans or whether drinking water provides the entire body burden.

Even if many food plants can be shown to absorb and retain perchlorate under some conditions, the primary source of this contaminant is irrigation water. However, merely exposing the growing plant to perchlorate does not imply absorption or accumulation in the edible portions. In the studies on uptake by lettuce seedlings, the plants have been subjected to perchlorate concentrations many times higher than those encountered in irrigation water. In addition, the confounding

factors described previously and the harvest conditions have not been accounted for.

Because aerospace industries, perchlorate manufacturers, and military bases that use perchlorate salts are fairly localized geographically, most of the country's agricultural products should be free from exposure via tainted irrigation water. On the other hand, some produce is largely supplied by regions that irrigate with Colorado River water, which is known to contain perchlorate. Therefore, such produce represents a *potential* exposure route for consumers. There are currently no investigations underway to examine food crops with documented exposure to perchlorate via irrigation or fertilization. In the meantime, the gathering of data by fertilizer manufacturers who choose to screen their finished products as part of routine quality control measures to prevent any recurrence of perchlorate contamination is welcome. Some state or local authorities (e.g., agriculture departments or state chemists' offices) may choose to conduct periodic screenings in the course of their normal operations of assaying fertilizers to validate the grade. Unfortunately, it is impossible to be more specific since the source of the contamination previously observed has never been identified, but appears to have reflected an episodic, if not isolated, incident. There is inadequate evidence to suggest widespread or long-term perchlorate contamination in fertilizers used for the bulk of production farming operations nationwide. In fact, most evidence points to the contrary, but a modest level of continued vigilance would not be inappropriate. While the likelihood of exposure via agricultural sources is small due to the low consumption of Chilean nitrate salts and the low perchlorate concentrations therein, the significance of whatever exposure does occur is unknown in terms of food plant uptake or ecological impact.

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