A Risk Management Approach to Fertilizer Safety

Prepared by
William C. Herz
Vice President, Scientific Programs
The Fertilizer Institute

Risk Management/Product Stewardship

- Risk management is the process in which information developed in the risk assessment process is utilized to make informed decisions about limiting risk through action.
- Risk management ultimately considers a broad variety of risk assessment data to inform the decision – making process.
- Risk management may relate solely to environmental or occupational health issues or in a broader context may be part of an overall corporate strategy (financial elements – insurance, hedging strategies, etc.)

- Stewardship involves looking around the curve and trying to preemptively predict the regulatory/political/economic trends and addressing in a voluntary manner

Product Stewardship/Sustainability

- Questions raised should include:
- Is our footprint as small as possible?
- Are all factors in balance – in our case; economic goals; environmental goals; and social goals

At the field level; **the 4R system is our answer**, based on agronomic and environmental science

- **Economic** – farming must be profitable. Healthy farm gate incomes are a good predictor of conservation practice implementation
- **Environmental** – are our production processes as efficient as they can be? Are we meeting environmental production regulatory goals? Are we minimizing our footprint on air and water quality?
- **Social** – Food production needs to double by approximately 2040. Increases in food prices disproportionately affect those in the lower socioeconomic spheres

Product Testing Program

First, Identify the Data Gaps

- Risks as characterized include:
-
- Lack of detailed information surrounding toxicology of fertilizer chemicals;
- Lack of comprehensive human health (toxicological) and ecological toxicity data and full characterization of non-nutritive elements in fertilizer (trace elements and possible contaminants); and
- These gaps made it impossible to perform an accurate risk assessment, leaving the industry unable to accurately estimate risks to applicators, farm families, and consumers

Other Issues

- Make the industry vulnerable to allegations from environmental groups and others regarding safety of products
- In addition, fertilizers are regulated in the U.S. at the state level
  - Many states were contemplating regulation of trace element levels and other contaminants; thus, development of a ‘uniform standard bill’ that states could adopt would prove useful
- Would help ensure a more consistent regulatory framework across states
- Led to the work in the trace elements (primarily heavy metals) research and the risk assessment program

TFI Response

- TFI embarked on a three pronged effort to ensure safety to all stakeholders in regard to the health and safety of commercial fertilizers. The three components of this program include:

- Development of Product Testing dossiers for 23 primary commercial fertilizers

- Evaluation of the elemental composition of fertilizers (North Carolina State University);

- Development of a risk assessment for both macro – and micronutrient products and develop scenarios for applicators and consumers

Product Testing: Program Description

- A TFI nine year program to develop and summarize screening-level hazard information for high production volume (HPV) chemicals
- Responds to both European Union Organization for Economic Cooperation and Development (EU OECD) and EPA HPV program requirements
- The EPA program began as a voluntary requirement; now it has become mandatory
- The OECD Screening Information Data Sets (SIDS) program is mandatory;

Product Testing: Program Description

- Much of the data has now been accepted will be used in the next phase of their chemical evaluation program - Registration, Evaluation, Authorization and Restriction of Chemicals (REACH) program
- The data elements include: physical - chemical characterization, environmental fate, mammalian toxicity and ecotoxicity
- Costs > $3 million; paid out of TFI general funds
- To avoid duplication of efforts and costs; European Fertilizer Manufacturers Association (EFMA) bought into the program three years ago

Product Testing: Program Overview

- A health and environmental safety data summary dossier was prepared for each of the 23 materials
- The dossiers summarize available literature, rating each reference as to overall reliability and quality (only 1 or a 2 are acceptable in OECD/EPA framework for generating conclusions
- Also contain new testing data, and provides a category description and read across data as well as provides a conclusion regarding the inherent hazards of the material
- As part of the package submitted to the OECD committee a summary document – SIAP is provided as well

Three Different Programs to Test Chemicals

- The International Council of Chemical Associations (ICCA) consists of chemical associations from the U.S., Canada, Europe, Japan, Australia, Mexico, Brazil, Argentina, and New Zealand. ICCA has an initiative on international HPV chemicals (*the fertilizers were on this list originally*)
- Environmental Protection Agency's (EPA) high production volume (HPV) program, (**focused on organic chemicals**) and
- Organisation For Economic Co-Operation And Development (OECD) Screening Information Data Set (SIDS) program within the European Union (EU).
- EU Program has now become REACH

Linkage Between International Programs

- There is consistency among the OECD HPV SIDS Program, the ICCA HPV Initiative, and the U.S. HPV Challenge Program. All three programs have the following components:
- Focus on HPV chemicals;
- Are based on the OECD SIDS test battery;
- Include the steps of information gathering, test plan development, and conducting the assessments
- SIDS testing on as needed basis to provide a complete set of screening level hazard data;
- Allow the use of category approaches to group chemicals and the use of Structure
- Activity Relationship (SAR) analysis as an alternative to testing where scientifically appropriate

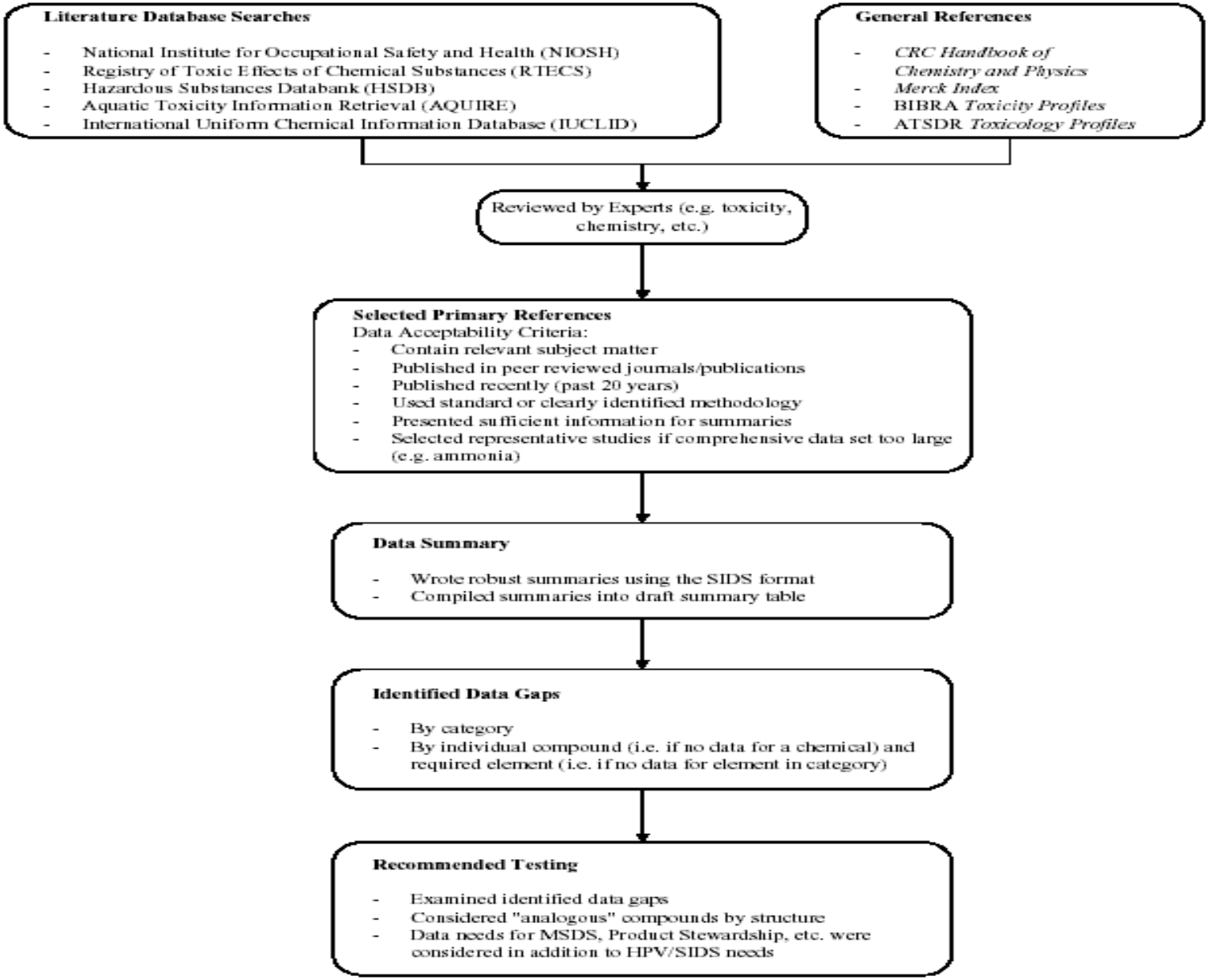
Product Testing: Studies Conducted

- Laboratories involved: Livermore in England and BioReliance in U.S. were utilized to perform the testing.
- Thirty-four new studies were conducted, including:
  - acute oral
  - acute dermal
  - mutagenicity
    - bacterial *in vitro*
    - non-bacterial *in vitro*
  - repeat dose (including developmental toxicity) evaluation
  - fish acute
  - algal toxicity

Chemicals Covered

Ammonia
Ammonium sulfate
Nitrogen solutions (UAN)
Sodium nitrate
Potassium nitrate
Diammonium phosphate
Triple super phosphate
Potassium chloride
Potassium sulfate
Calcium sulfate
Phosphoric acid
Calcium ammonium nitrate (CAN)
Aqua ammonia
Ammonium phosphate sulfate
Urea
Potassium sodium nitrate
Monoammonium phosphate
Single super phosphate
Liquid polyphosphate
Nitric acid
Potassium magnesium sulfate
Sulfuric acid
Calcium nitrate fertilizer

FIGURE 1. TESTING PLAN FLOW-DIAGRAM



Category Approach: Description

- The fertilizer chemicals were divided into five categories (i.e., ammonia compounds, nitrate compounds, phosphate compounds, sulfates, and acids)

- <u>The benefits of this approach include</u>:
- Data can be pooled;
- Resources are optimized;
- Fewer animals are used in testing (EPA, OECD and environmentalists recommend minimizing animals sacrificed),
- Do not lose the ability to evaluate the hazards and safety of the individual chemicals.

Categories

CATEGORY	COMPOUND	CAS NUMBER
Ammonia Compounds	Anhydrous ammonia	7664-41-7
	Aqua ammonia	1336-21-6
	Ammonium nitrate	6484-52-2
	Ammonium sulfate	7783-20-2
	Ammonium thiosulfate	7783-18-8
	Nitrogen solutions (UAN)*	15978-77-5
	Ammonium phosphate sulfate	12593-60-1
	Diammonium phosphate (DAP)	7783-28-0
	Monoammonium phosphate (MAP)	7722-76-1
	Urea	57-13-6

Categories

CATEGORY	COMPOUND	CAS NUMBER
Nitrate Compounds	Sodium nitrate	7631-99-4
	Ammonium nitrate	6484-52-2
	Potassium nitrate	7757-79-1
	Potassium sodium nitrate	7757-79-1/7631-99-4
	Nitrogen solutions (UAN)*	15978-77-5
	Calcium nitrate fert	No CAS
	Calcium Ammonium Nitrate	No CAS

Categories

CATEGORY	COMPOUND	CAS NUMBER
Phosphate Compounds	Diammonium phosphate (DAP)	7783-28-0
	Monoammonium phosphate (MAP)	7722-76-1
	Liquid polyphosphate	--
	Single superphosphate**	8011-76-5
	Triple superphosphate**	65996-95-4

Categories

CATEGORY	COMPOUND	CAS NUMBER
Sulfates	Potassium magnesium sulfate Potassium sulfate Calcium sulfate	17855-14-0 7778-18-9 7778-80-5
Acids	Phosphoric acid Nitric acid Sulfuric acid	7664-38-2 7697-37-2 7664-93-9

Summary: Approach Utilized

- All new studies were conducted according to OECD and EPA testing guidelines and protocol
- Chemicals studied using a category approach to minimize costs, reduce animals sacrificed and extrapolate results among like chemicals
- Twenty-three materials in five categories (i.e., Ammonia Compounds, Nitrate Compounds, Phosphate Compounds, Sulfates, and Acids) were evaluated through this program.
- Twenty-two dossiers were generated – GTSP and SSP were combined in one document.
- The calcium nitrate compounds were added after the fact – no toxicological testing was performed on these compounds but the functional group is the nitrate molecule

OECD Regulatory Review

- OECD committee review of chemicals occurs in Paris in the spring and Helsinki, Finland in the fall
- April, 2007 the phosphate and ammonia group received final approval (SIAM 24)
- October, 2007 the nitrate and sulfate group received final approval (SIAM 25)
- April, 2008 acid group (nitric only) approved

U.S. Regulatory Requirements: OSHA

- Upon receipt of this data a 90 calendar day regulatory trigger starts within which you must update your material safety data sheets (MS-DS)
- Upon first product shipment you must also notify your distributors once the chemical – specific MS-DS has been updated
- These regulatory requirements are based on requirements found in the Occupational Safety and Health Administration "Hazard Communication Standard"
- OSHA currently has a notice of proposed rulemaking out to harmonize hazcom stds with international
- Ammonia – skull and crossbones?

Benchmarks Utilized

- Toxicity scales were employed based on U.S. EPA protocol from the Federal Insecticide, Fungicide and Rodenticide Act (FIFRA).
- A consistent benchmark is important so companies are using similar language on MS-DS and regulatory submissions.

Aquatic Toxicity

EC/LC50 (mg/L)	**Toxicity Description**
<0.1	Very Highly Toxic
0.1-1	Highly Toxic
1-10	Moderately Toxic
10-100	Slightly Toxic
>100	Practically Non-Toxic

Benchmarks: Mammalian Toxicity

Toxicity Category	I	II	III	IV
Toxicity Rating	High	Moderate	Low	Very Low
Oral LD_{50}	≤ 50 mg/kg	>50-500 mg/kg	>500-5000 mg/kg	>5000 mg/kg
Dermal LC_{50}	≤ 200 mg/kg	>200-2000 mg/kg	>2000-20,000 mg/kg	>20,000 mg/kg
Inhalation LC_{50}	≤ 0.2 mg/L	>0.2-2 mg/L	>2-20 mg/L	>20 mg/L

Product Testing: Results

- Most products tested fell into the low to very low category for mammalian tests conducted.

- Most products also fell into the practically non-toxic to slightly toxic categories for aquatic toxicity tests (ratio of 10 - > 100).

- Known exceptions include inhalation toxicity associated with ammonia, dermal and inhalation toxicity associated with sulfuric acid and nitric acid.

Project 2: TFI Trace Element Research

- DAP — Di-ammonium Phosphate
- MAP — Mono-ammonium phosphate
- AS — Ammonium Phosphate
- KCl — Potassium Chloride (red)
- P Rock — Phosphate Rock
- TSP — Triple Super Phosphate
- SSP — Single Super Phosphate
- Urea — (granular and prill)
- AN — Ammonium Nitrate
- KMAG — Potassium/Magnesium Sulfate
- UAN — Urea/Ammonium Nitrate (liquid)
- NH3 — Ammonia

Taking a Representative Sample?

- Most production facilities operate all year
- For given time period (e.g. 30 days) all production facilities contribute to total amount of fertilizer source material produced
- Sampling of facilities weighted by projected contribution to total amount of fertilizer source material produced in a given time period
- Results cover greater than 90% of agriculturally applied fertilizer in the United States!

Trace Elements Research Objectives

1. Statistically valid sampling of all TFI member fertilizer source material production facilities to generate composite samples representative of different fertilizer source materials

2. Conduct chemical analysis of the composite samples using modern chemical instrumentation and a defensible quality control/quality assurance program

Sampling Scheme: Objectives and Approach

- Based on inductive statistical procedures ('population' and random samples)
- Mean value is important because fertilizer source material is mainly dispersed in bulk, not as individual units
- Focus on mean concentration allows compositing (reducing analytical burden and cost), so emphasis is NOT on range of concentrations in individual units
- Most production facilities operate all year
- For given time period (e.g. 30 days) all production facilities contribute to total amount of fertilizer source material produced
- Sampling of facilities weighted by projected contribution to total amount of fertilizer source material produced in a given time period

Sampling Scheme: Approach

- For a given sampling period, the methodology requires:
  - Total # facilities for a certain material
  - Region in N. America where facility is located
  - Typical daily production rate (24 hour period)
- Attempt to sample twice in 365-day period to estimate long-term temporal variance in mean concentrations
- Primary drawback in this approach – loss of variance and range given geographical and plant specific variation

Elements Studied

- **Micronutrients***: Boron, **Cobalt**, **Copper**, Iron, Manganese, **Molybdenum**, **Selenium**, **Zinc**

- **Trace Metals**: Antimony, **Arsenic**, Beryllium, Bismuth, **Cadmium**, **Chromium**, **Lead**, **Mercury**, **Nickel**, Silver, Thallium, **Vanadium**

- **Radionuclides**: Radium, Uranium, Thorium

- **Other**: Aluminum, Barium, Strontium, Titanium

* **Bold** indicates those elements also covered by the TFI risk assessment

TFI Risk Assessment Program

- Primary author is Dr. Daniel Woltering of the Weinberg Group. The risk assessment is necessitated for the following reasons:

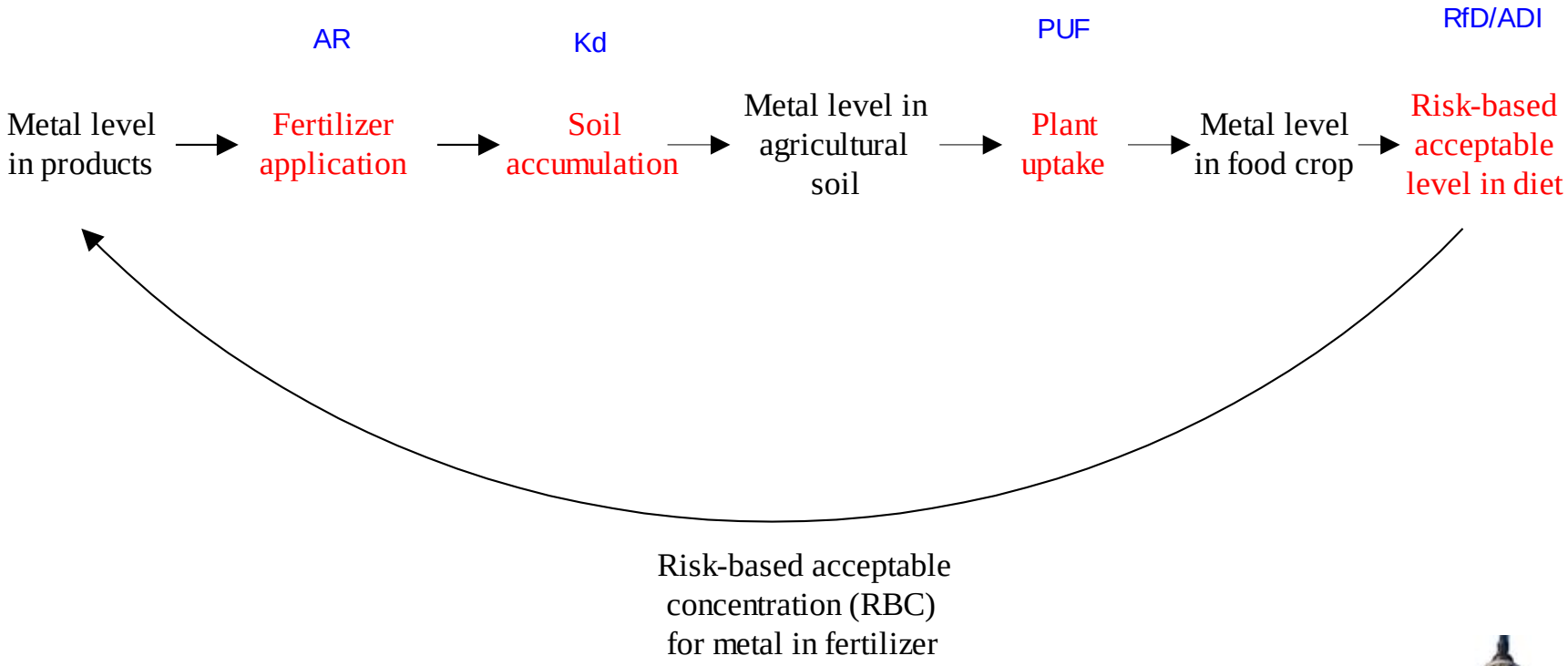
- Product stewardship;
- Address concerns raised about metals;
- Prevailing scientific standard to judge health and environmental safety of chemicals;
- Provides basis for risk management; and
- Answers for applicators, farmers and public.

Scope of the Risk Assessment

- NPK and phosphate products plus boron, iron, manganese, zinc micronutrient products
- Post application
- Health risks
- Farm family
- Crop ingestion, soil ingestion, dermal contact

- 9 metals
  - As, Cd, Co, Pb, Hg, Mo, Ni, Se, Zn

Conceptual Model



Risk – based Numbers

TABLE 14
UNIT RISK BASED CONCENTRATIONS (RBCs) (a) FOR ALL SCENARIOS

MOPC	Adult Farm Resident RBC				Child Farm Resident RBC				Lowest Unit RBC (b)	
	Vegetable	Roots	Grains	Multi-crop	Vegetable	Roots	Grains	Multi-crop	Scientific Notation	Standard Notation
Phosphate Fertilizer										
Arsenic (c)	9.9E+00	5.4E+01	9.4E+00	**4.5E+00**	2.7E+01	9.7E+01	1.7E+01	9.8E+00	4.5E+00	4.5
Cadmium	1.1E+02	2.0E+02	1.5E+02	4.9E+01	6.4E+01	9.8E+01	5.4E+01	**2.3E+01**	2.3E+01	23
Chromium (III)	1.8E+06	1.4E+06	1.1E+05	1.0E+05	1.7E+05	1.3E+05	3.6E+04	**3.4E+04**	3.4E+04	34,000
Cobalt	4.5E+04	6.6E+04	1.2E+04	8.4E+03	1.5E+04	1.5E+04	4.0E+03	**3.1E+03**	3.1E+03	3,100
Copper	7.0E+04	1.1E+04	8.2E+02	7.6E+02	2.0E+04	5.0E+03	3.0E+02	**2.8E+02**	2.8E+02	280
Lead	1.3E+03	2.0E+03	2.1E+02	1.6E+02	7.7E+02	9.3E+02	8.5E+01	**7.3E+01**	7.3E+01	73
Mercury	1.5E+01	1.3E+01	3.3E+00	2.2E+00	7.8E+00	6.1E+00	1.2E+00	**9.0E-01**	9.0E-01	0.9
Molybdenum	3.3E+02	2.2E+03	1.6E+02	1.0E+02	1.8E+02	9.0E+02	5.6E+01	**4.2E+01**	4.2E+01	42
Nickel	3.8E+03	5.4E+03	1.4E+03	1.0E+03	9.9E+02	9.3E+02	4.5E+02	**3.5E+02**	3.5E+02	350
Selenium	2.6E+03	2.9E+03	3.8E+02	3.0E+02	1.5E+03	1.4E+03	1.4E+02	**1.2E+02**	1.2E+02	120
Vanadium	3.6E+04	2.9E+04	1.0E+04	8.3E+03	4.2E+03	3.2E+03	2.8E+03	**2.2E+03**	2.2E+03	2,200
Zinc	1.5E+04	5.3E+04	4.2E+03	3.1E+03	8.8E+03	2.5E+04	1.5E+03	**1.2E+03**	1.2E+03	1,200
Micronutrient Fertilizer										
Arsenic (c)	1.2E+02	8.4E+02	5.9E+01	**3.8E+01**	3.2E+02	1.5E+03	1.0E+02	7.4E+01	3.8E+01	38
Cadmium	1.3E+03	3.1E+03	9.5E+02	4.7E+02	7.6E+02	1.5E+03	3.4E+02	**2.1E+02**	2.1E+02	210
Chromium (III)	2.1E+07	2.1E+07	6.7E+05	6.7E+05	2.1E+06	2.1E+06	**2.2E+05**	**2.2E+05**	2.2E+05	220,000
Cobalt	5.4E+05	1.0E+06	7.3E+04	6.2E+04	1.8E+05	2.3E+05	2.5E+04	**2.3E+04**	2.3E+04	23,000
Copper	8.3E+05	1.8E+05	5.2E+03	5.0E+03	2.3E+05	7.8E+04	1.9E+03	**1.8E+03**	1.8E+03	1,800
Lead	1.6E+04	3.1E+04	1.3E+03	1.2E+03	9.1E+03	1.5E+04	5.4E+02	**5.0E+02**	5.0E+02	500
Mercury	1.7E+02	2.0E+02	2.1E+01	1.7E+01	9.3E+01	9.5E+01	7.4E+00	**6.5E+00**	6.5E+00	6.5
Molybdenum	3.9E+03	3.5E+04	9.8E+02	7.6E+02	2.2E+03	1.4E+04	3.5E+02	**3.0E+02**	3.0E+02	300
Nickel	4.6E+04	8.4E+04	9.0E+03	7.5E+03	1.2E+04	1.4E+04	2.9E+03	**2.6E+03**	2.6E+03	2,600
Selenium	3.1E+04	4.6E+04	2.4E+03	2.1E+03	1.7E+04	2.2E+04	8.7E+02	**8.0E+02**	8.0E+02	800
Vanadium	4.2E+05	4.5E+05	6.4E+04	5.9E+04	5.0E+04	5.1E+04	**1.7E+04**	**1.7E+04**	1.7E+04	17,000
Zinc	1.8E+05	8.3E+05	2.6E+04	2.3E+04	1.0E+05	4.0E+05	9.6E+03	**8.6E+03**	8.6E+03	8,600

Notes:

Bold = Lowest RBC

MOPC = Metal of Potential Concern

(a) The units for all RBCs are mg MOPC/kg product (i.e., ppm). The lowest unit RBC for each metal is shown in the two far right columns. This is the value used for screening (presented in Section 4.0).

(b) The lowest unit RBC is the lowest for child and adult farm residents.

(c) The RBCs presented for arsenic are based on cancer. All other RBCs are based on non-cancer.

Risk Assessment Methodology

- 'Screening level assessment'
  - risks are more likely overestimated, not underestimated
- USEPA type models and algorithms
- Reasonable maximum exposure parameters
- Published toxicity values (RfD, ADI)
- Cancer and non-cancer endpoints
- Include range of AF, SACF, PUF values

Risk – based Numbers

Metal	2000 Draft Values		2001 Final Values	
	NPK Products (@1% P_2O_5)	Micronutrients (@1% Fe, Mn or Zn)	NPK Products (@1% P_2O_5)	Micronutrients (@1% Fe, Mn or Zn)
Arsenic	19	155	13	112
Cadmium	16	134	10	83
Cobalt	3,100	23,000	**136**	**2228**
Lead	97	738	61	463
Mercury	1	6	1	6
Molybdenum	42	300	42	300
Nickel	350	2,600	250	1,900
Selenium	120	800	26	180
Zinc	1,200	8,600	420	2,900

All units are mg/kg (ppm).
The principal difference between NPK and micronutrient RBCs is the difference in application rate for those products.

“Fertilizers are Safe”

- USEPA 1999
  - 9 metals; 260 samples of 13 NPK and micro products
  - All NPK products pass screen; arsenic in a few micronutrient samples did not pass screen
- CDFA 1999
  - RBCs for As, Cd, Pb in NPK and micro products
- TFI 2000 (draft)
  - RBCs for 12 metals and radium
  - All 925 samples of NPK products passed screen
  - All but 12 of 140 micro samples passed screen. [As and Pb in a few products]

Conclusion

- International regulations surrounding use of high production volume chemicals continue to increase

Future Directions and Challenges

- China's recently issued standard for metals
- European Union standards for metals
- Scope Risk Assessment Meeting: Continue to improve the science of cadmium uptake and environmental fate