
# The History of Ammonia to 2012

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Vice President, Economic Services
The Fertilizer Institute

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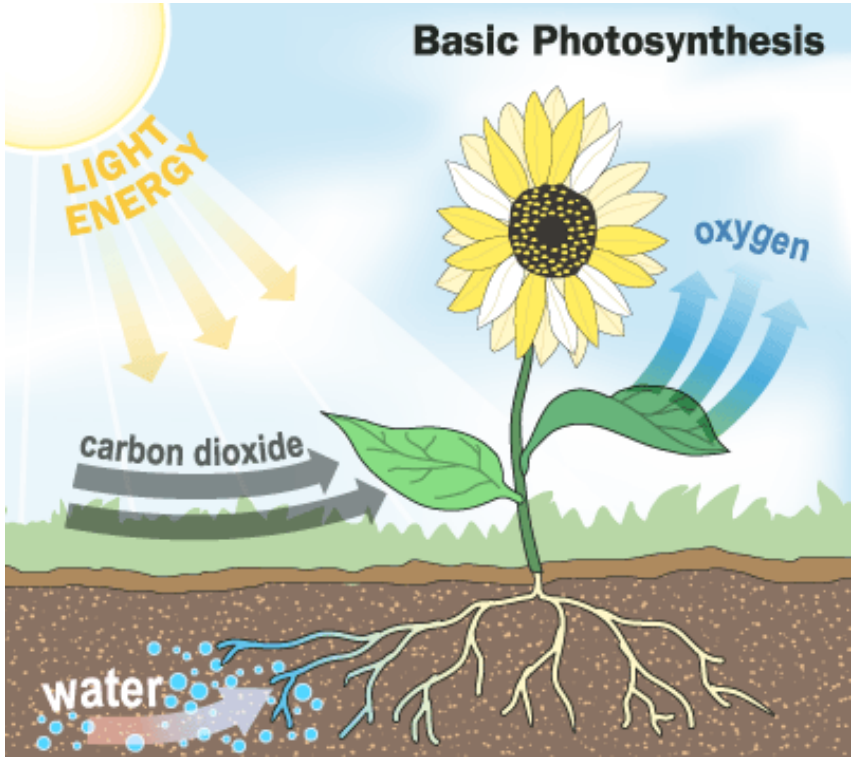
www.tfi.org

# Presentation Outline

- Nitrogen Before Haber-Bosch Ammonia
- Fritz Haber, Carl Bosch, BASF and Anhydrous Ammonia
- Haber-Bosch Ammonia Production Starts
- Ammonia Production Expands
- Nitrogen Demand – Global and U.S. Profile
- Importance of Haber-Bosch N (nutrients) to mankind

# 1770's - Birth of Modern Chemistry

**Joseph Priestly**
**English Minister**
**(1733 – 1804)**




**Jan Ingenhousz**
**Dutch Physician**
**(1730 – 1799)**

## Discovered the Fundamentals of Photosynthesis

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Source: Enriching the Earth, Vaclav Smil, 2001.

# 1770's - Birth of Modern Chemistry

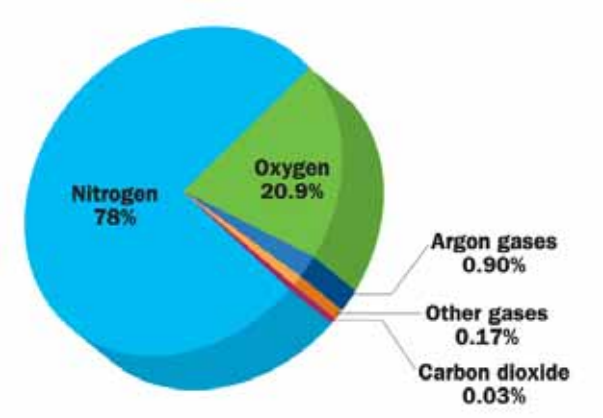
**Carl Wilhelm Scheele**
**Swedish Chemist**
**(1742 – 1786)**

**Daniel Rutherford**
**English Botanist**
**(1749 – 1819)**

**"discovered" N**

**Antoine Laurent Lavoisier**
**French Chemist**
**(1743 – 1794)**

**named "azote"**




## First Realization that Nitrogen Makes up Most of the Atmosphere

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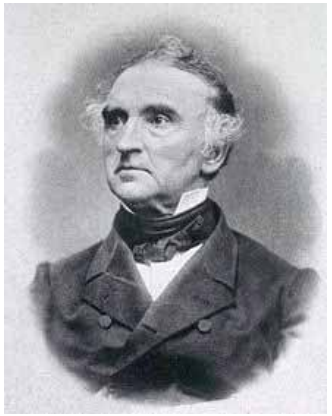
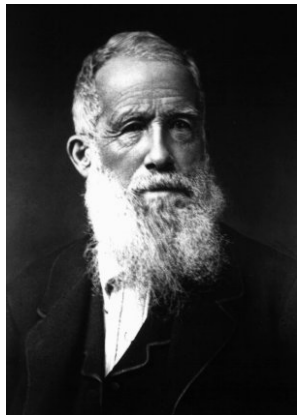
Source: Smil, 2001.

# 1800's - Value of N in Crop Production Demonstrated

Jean-Baptists Boussingault
French Chemist
(1802 – 1887)

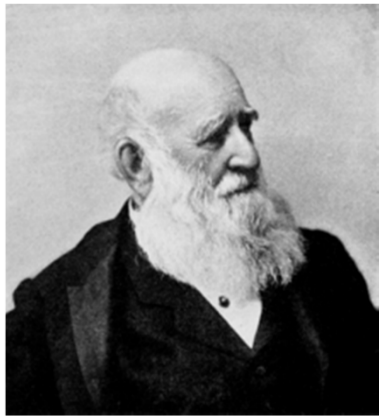


Justin von Liebeg
German Chemist
(1803 – 1873)



John Bennet Lawes
English Scientist
(1814 – 1900)

**Scientific Experiments Left No Doubt About Nitrogen's Crucial Role in Crop Production!**



Joseph Henry Gilbert
English Chemist
(1817 – 1901)

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Source: Smil, 2001.

# Birth of Anhydrous Ammonia – $NH_3$

**Claude-Louis Berthollet**
**French Chemist**
**(1748 – 1822)**

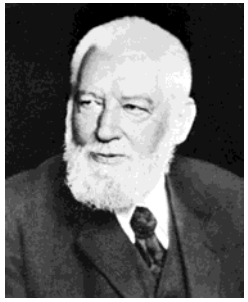
**1784 – Berthollet becomes aware that the element "azote" joins with hydrogen to form ammonia**

**Georg Friedrich Hildebrand**
**German Professor**
**(1764 - 1816)**

**1795 – The first failed attempt to combine N and H**

**More than a dozen chemists**

**1800's – Conducted experiments to synthesize ammonia**



**Wilhelm Ostwald**
**German Chemist**
**(1853 – 1932)**

**1900 – Ostwald though he had succeeded in synthesizing ammonia**
**– Tests by Carl Bosch for BASF proved him wrong; $NH_3$ production was result of contaminants in machine**

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Source: Smil, 2001, The Alchemy of Air, Thomas Hager, 2008.

# Nitrogen Sources: Pre Haber-Bosch

**Manures (barnyard and other)**

**Guano (solidified bird excrement accumulated on subtrop/tropical islands)**

**Chilean Nitrate (sodium nitrate)**

**Coke-Oven Gas (by-product) Ammonium Sulfate**

- Coke oven gases produced primarily in the steel industry
- Produced by reacting recovered coke oven ammonia with sulfuric acid

**Nitrogen Fixation Processes:**

- Electric Arc Process (1901 – Niagara Falls)

  Uses electrical current to combine N and oxygen in the air to form nitric oxide (NO)

  (NO) ➔ Nitric Acid ➔ Calcium Nitrate/Sodium Nitrate

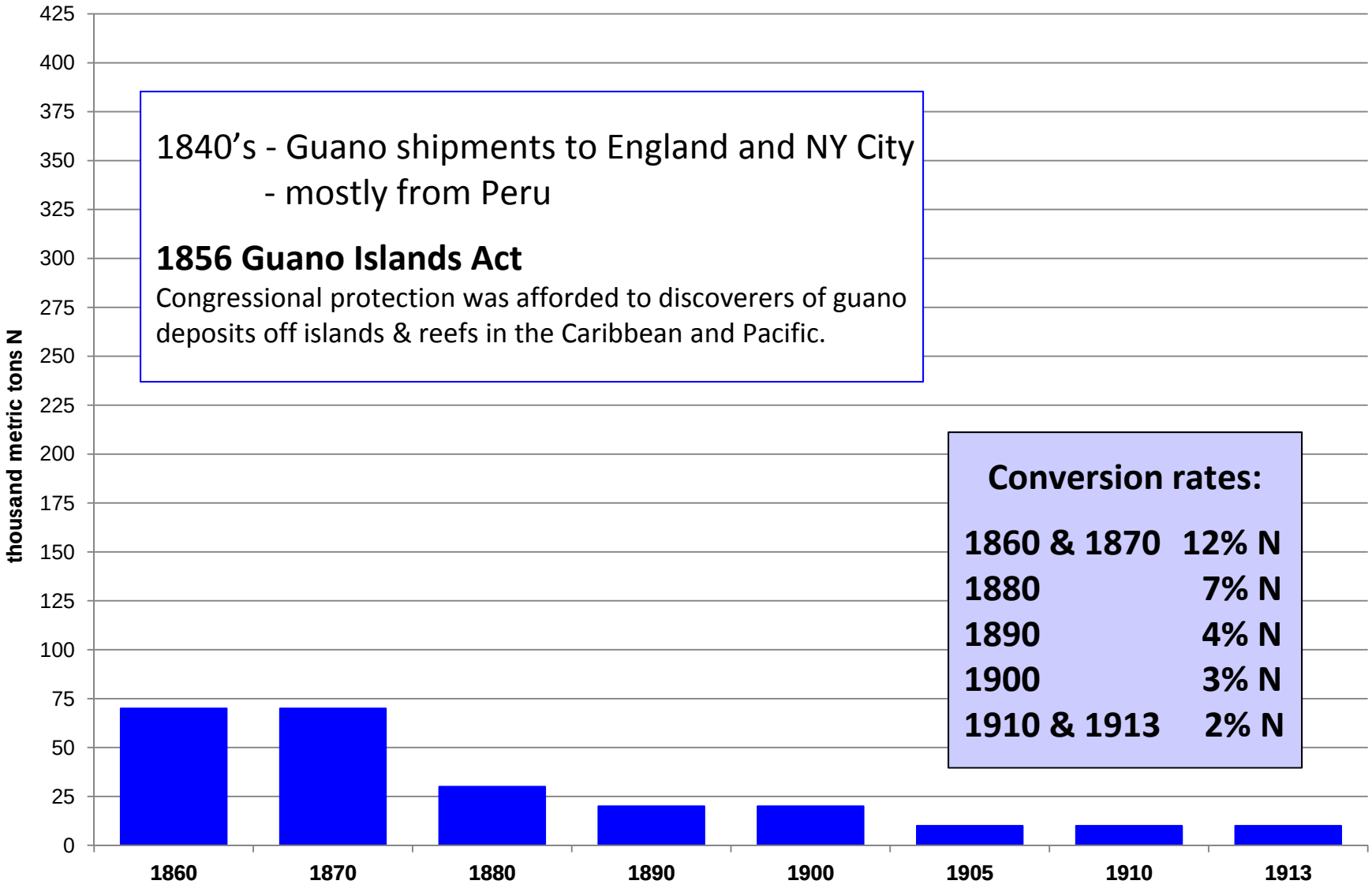
- Cyanamide Process (1907 – Italy)

  Limestone burned to form calcium oxide; fused with coke in electric furnace ➔ calcium carbide
  Calcium carbide ($CaC_2$) reacted with N at high temperature to form calcium cyanamide ($CaCN_2$)
  Calcium cyanamide ($CaCN_2$) ➔ ammonia; ammonium phosphates; nitric acid; ammonium nitrate



Source: Smil, 2001.

# N Production as Guano Extraction, Pre Haber-Bosch




1840's - Guano shipments to England and NY City
- mostly from Peru

**1856 Guano Islands Act**

Congressional protection was afforded to discoverers of guano deposits off islands & reefs in the Caribbean and Pacific.

**Conversion rates:**

| | |
|---|---|
| 1860 & 1870 | 12% N |
| 1880 | 7% N |
| 1890 | 4% N |
| 1900 | 3% N |
| 1910 & 1913 | 2% N |

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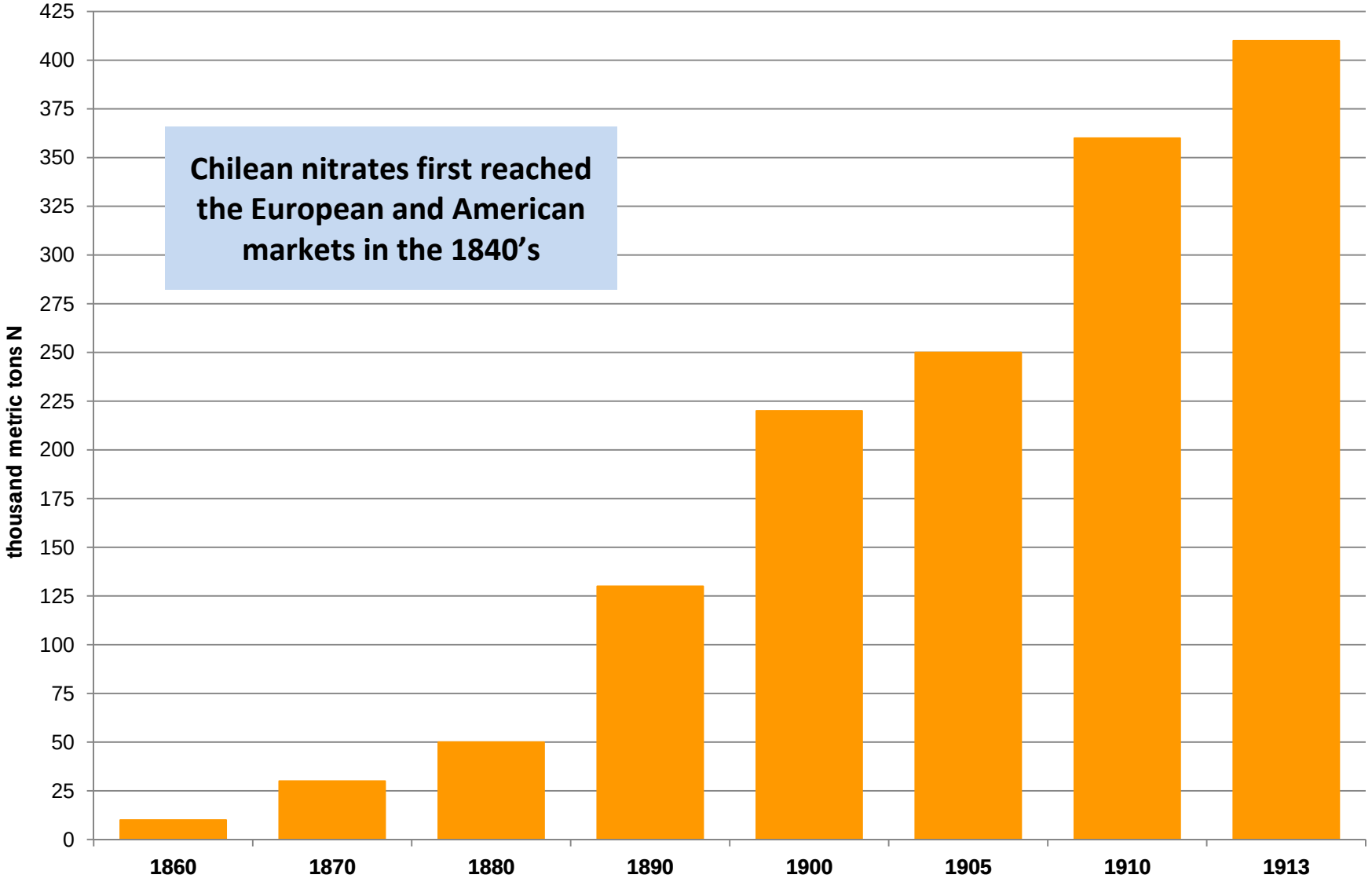
Source: Hager, 2008; Smil, 2001.

# Chilean Nitrate Production, Pre Haber-Bosch

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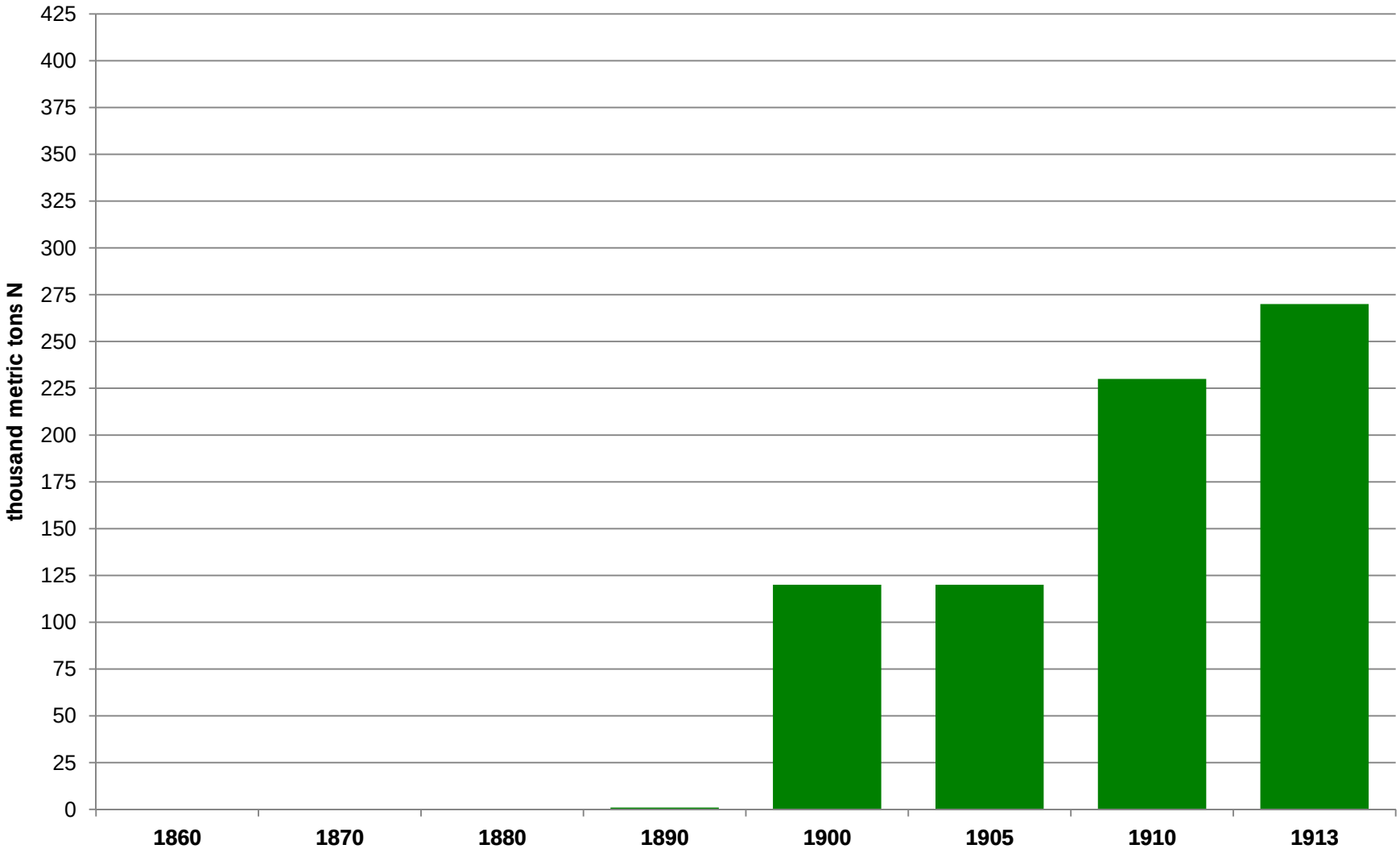
Source: Smil, 2001.

# Coke-oven Gas (by-product) AS

## Production, Pre Haber-Bosch

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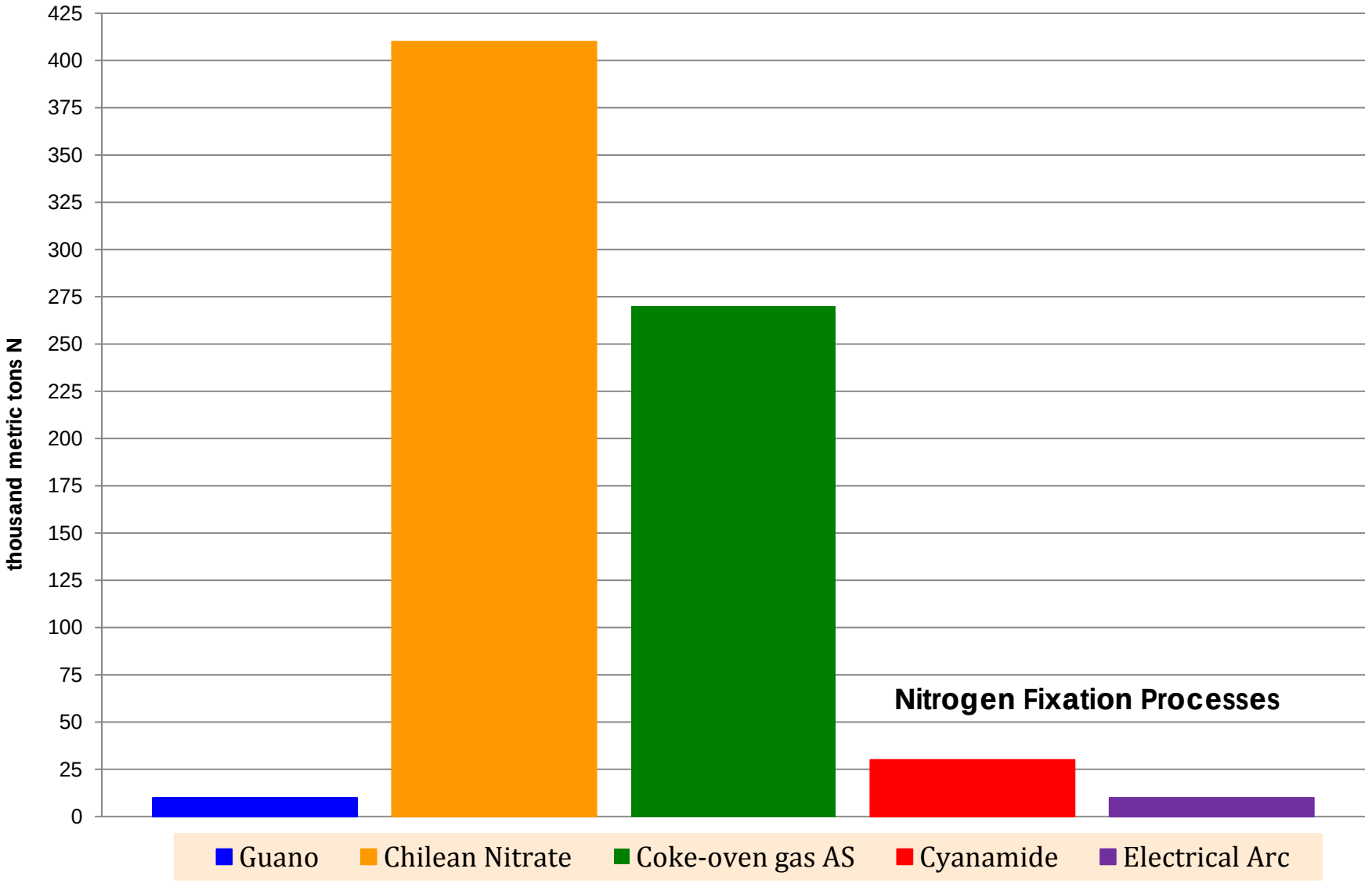
Source: Smil, 2001.

# Pre Haber-Bosch N Production, Excluding Ammonia - 1913

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Source: Smil, 2001.

# Evaluating Haber's Machine

Heinrich von Brunck
CEO of BASF

August Bernthsen
BASF Director of Research

Carl Bosch
BASF Chemist


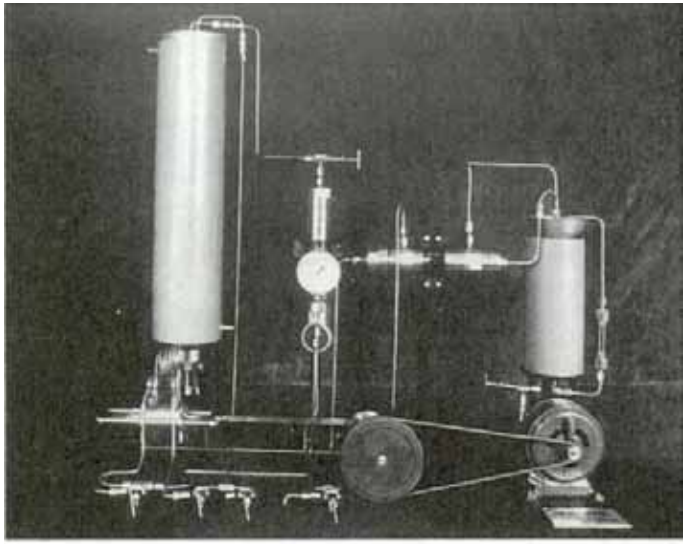

*Abb. 4 Haber-Le Rossignol-Apparatur zur Ammoniaksynthese*

Fritz Haber

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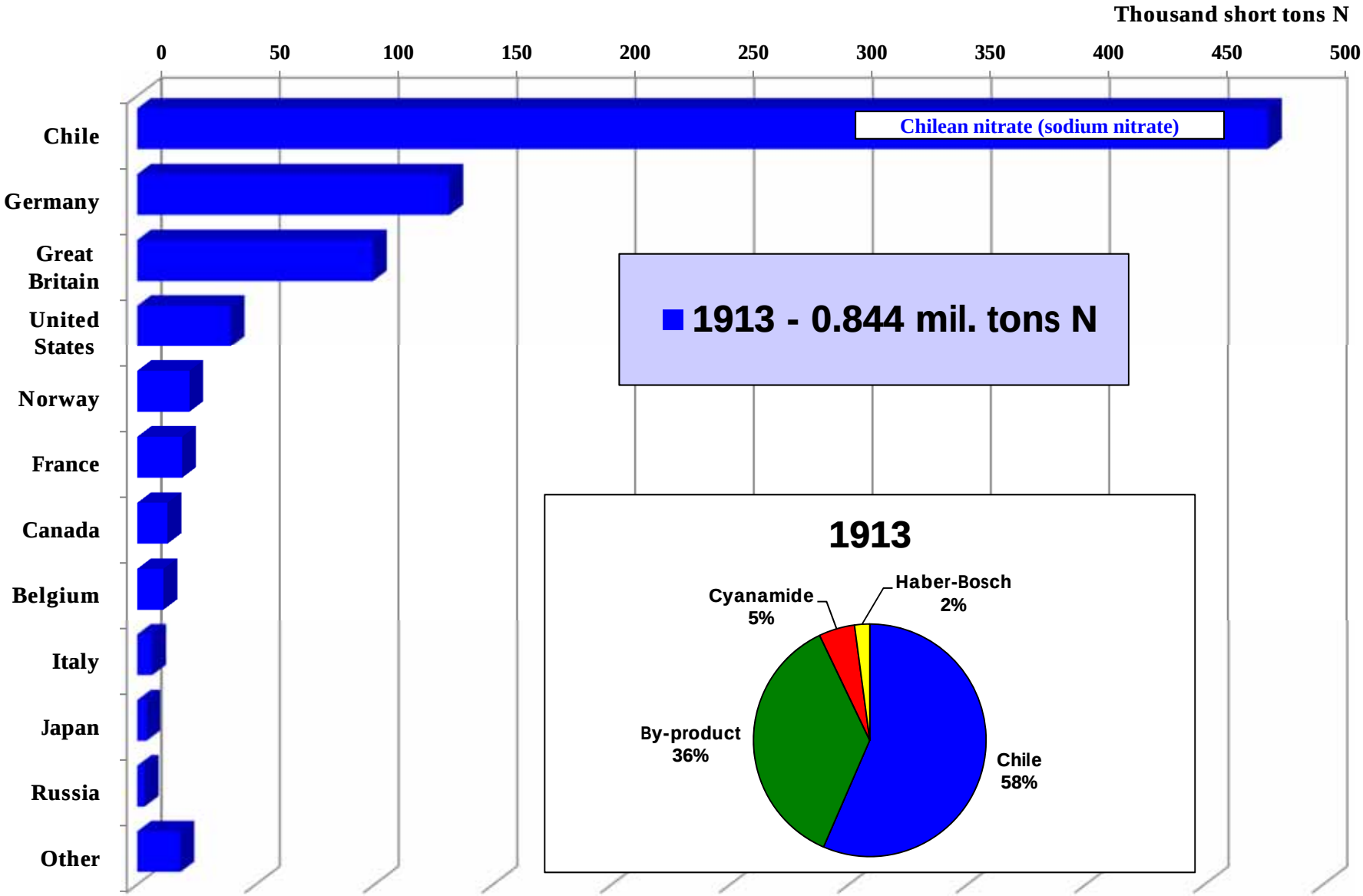
# Global N Production

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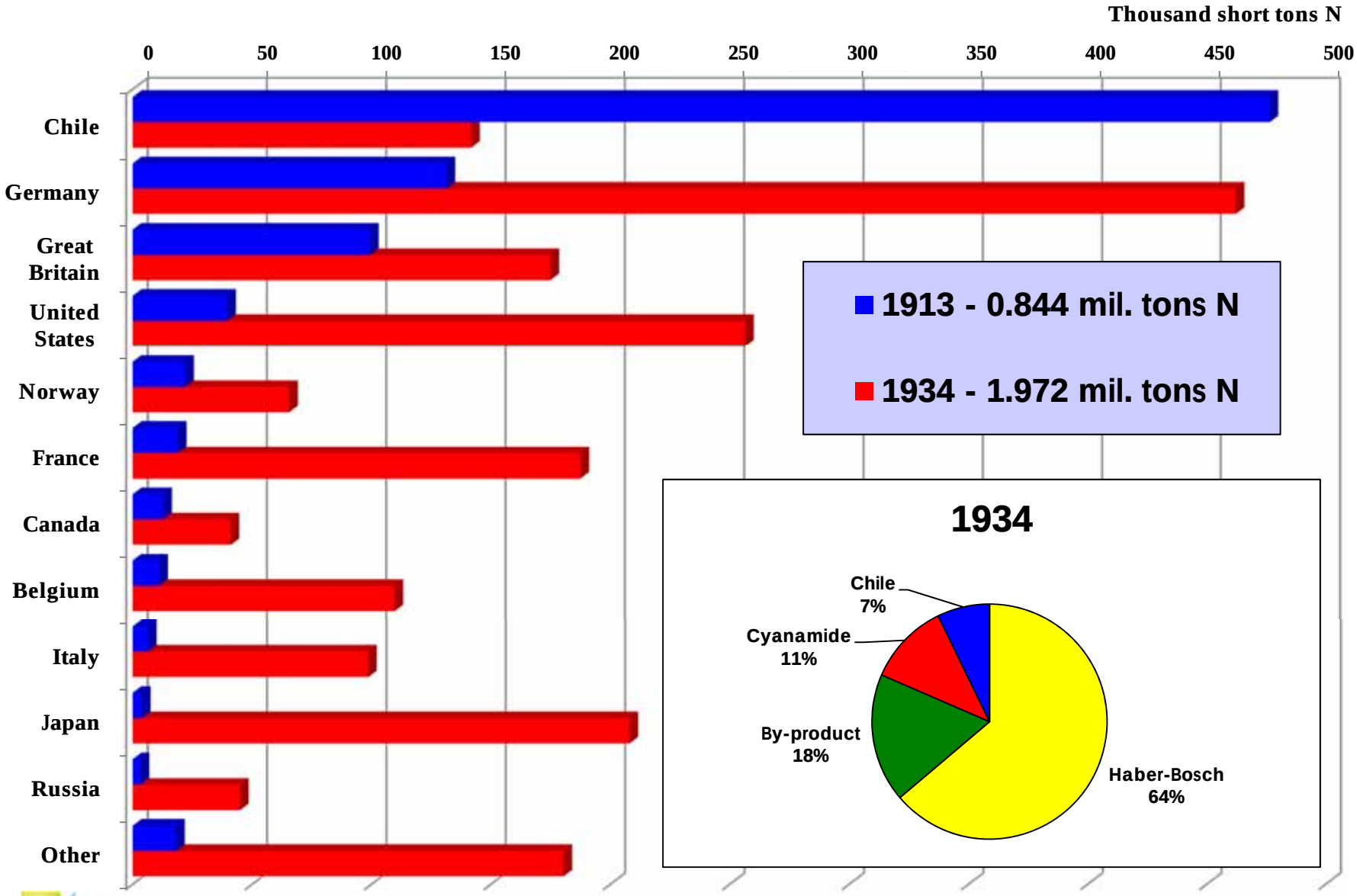
Source: Morrison, 1937.

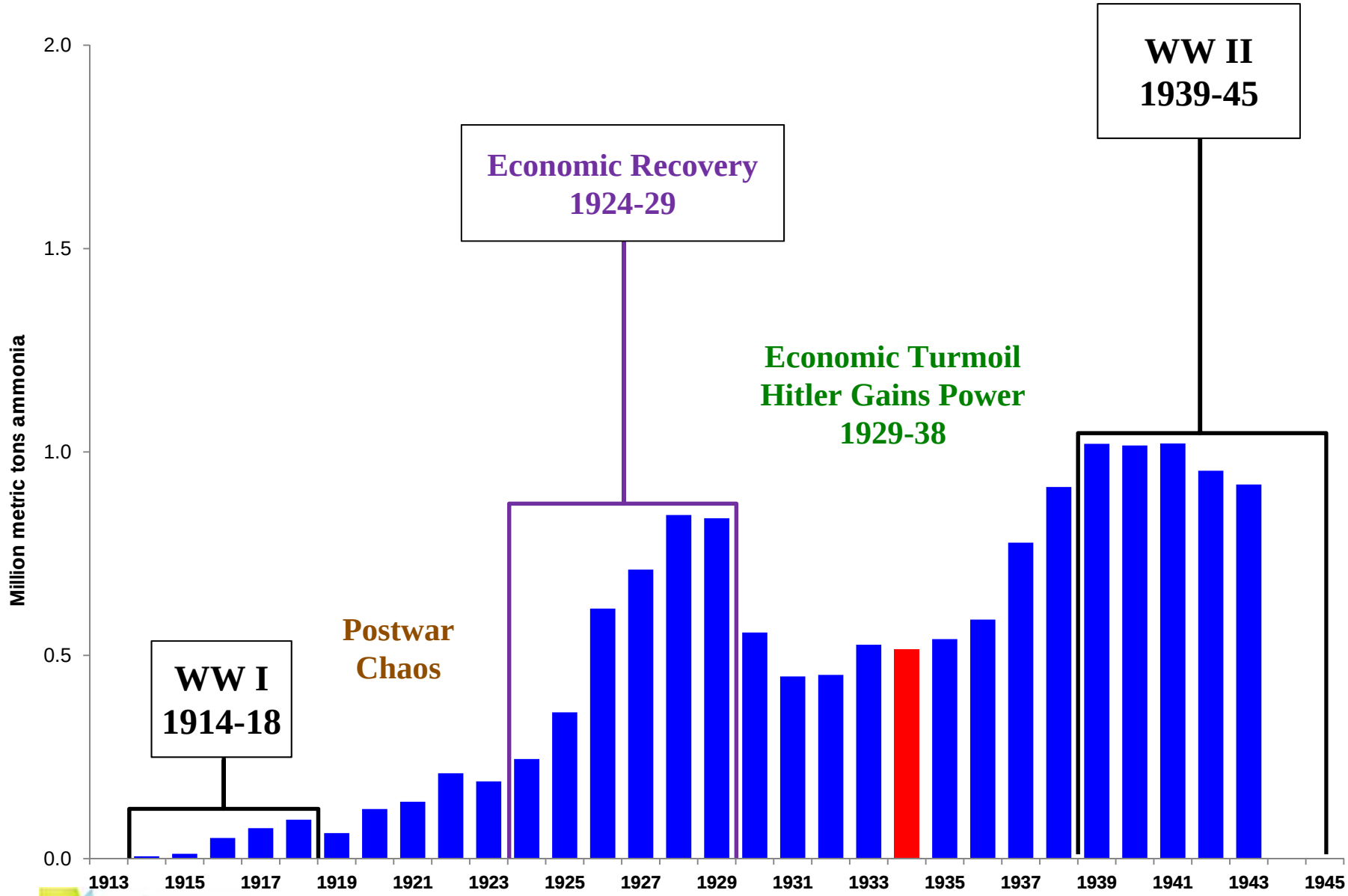
# Global N Production




The Fertilizer Institute

Source: Morrison, 1937.

# German Haber-Bosch Ammonia Production

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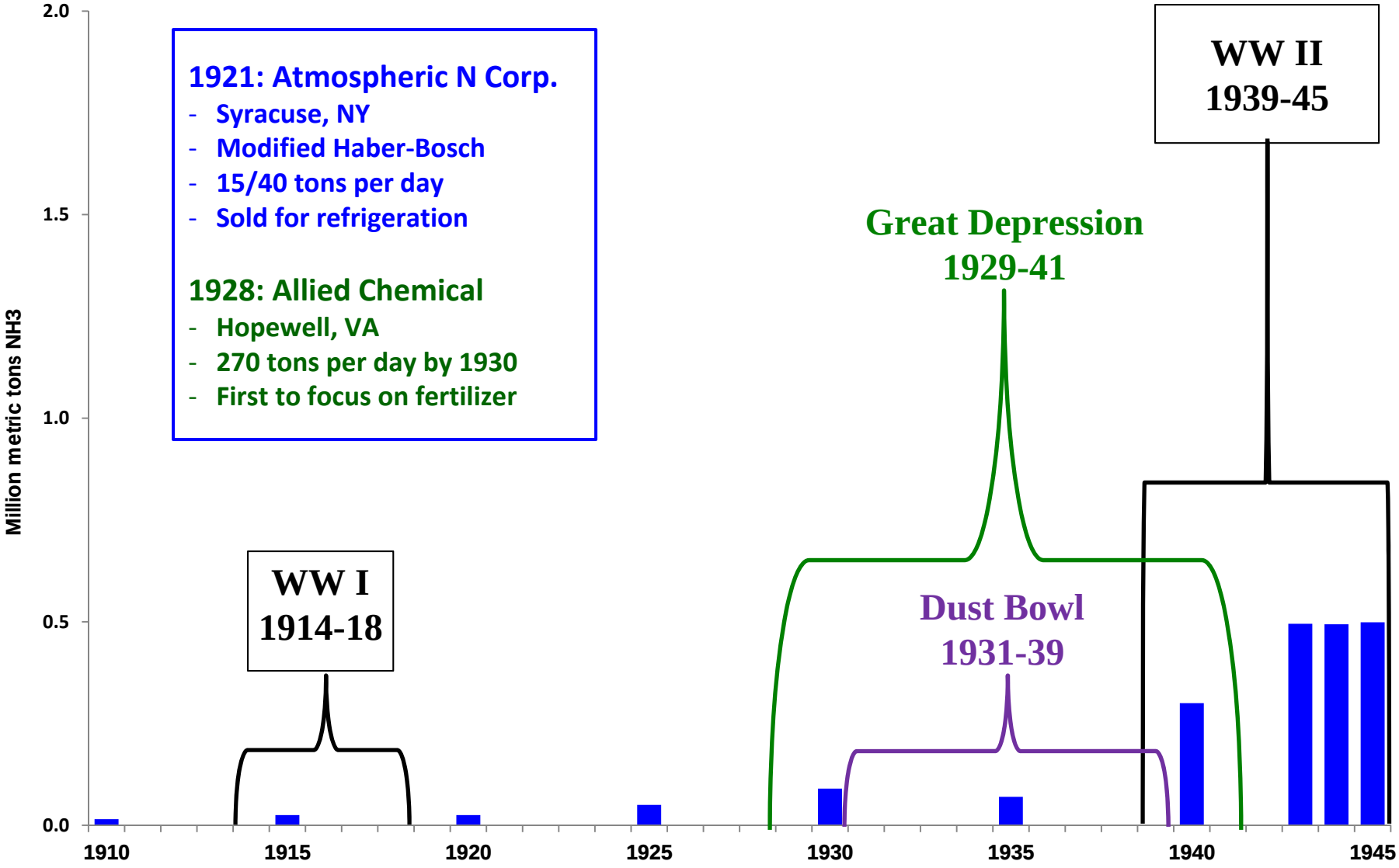
Source: Ammonia production data taken from Smil, 2001.

# U.S. Ammonia Production

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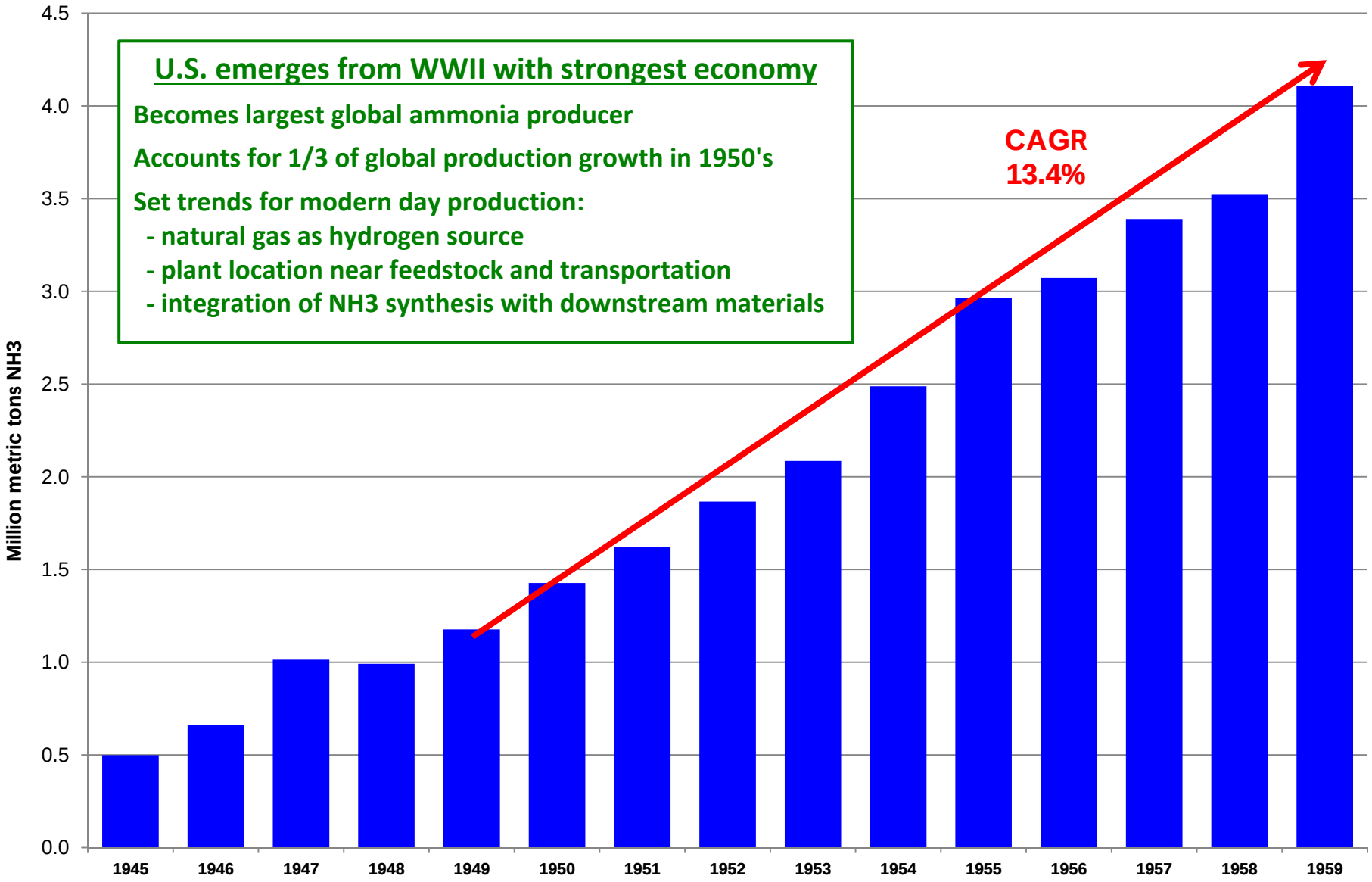
Source: Nelson, 1990; Data: 1910-1940 - Smil, 2001; 1943-1945 - U.S. Geological Survey.

# U.S. Ammonia Production

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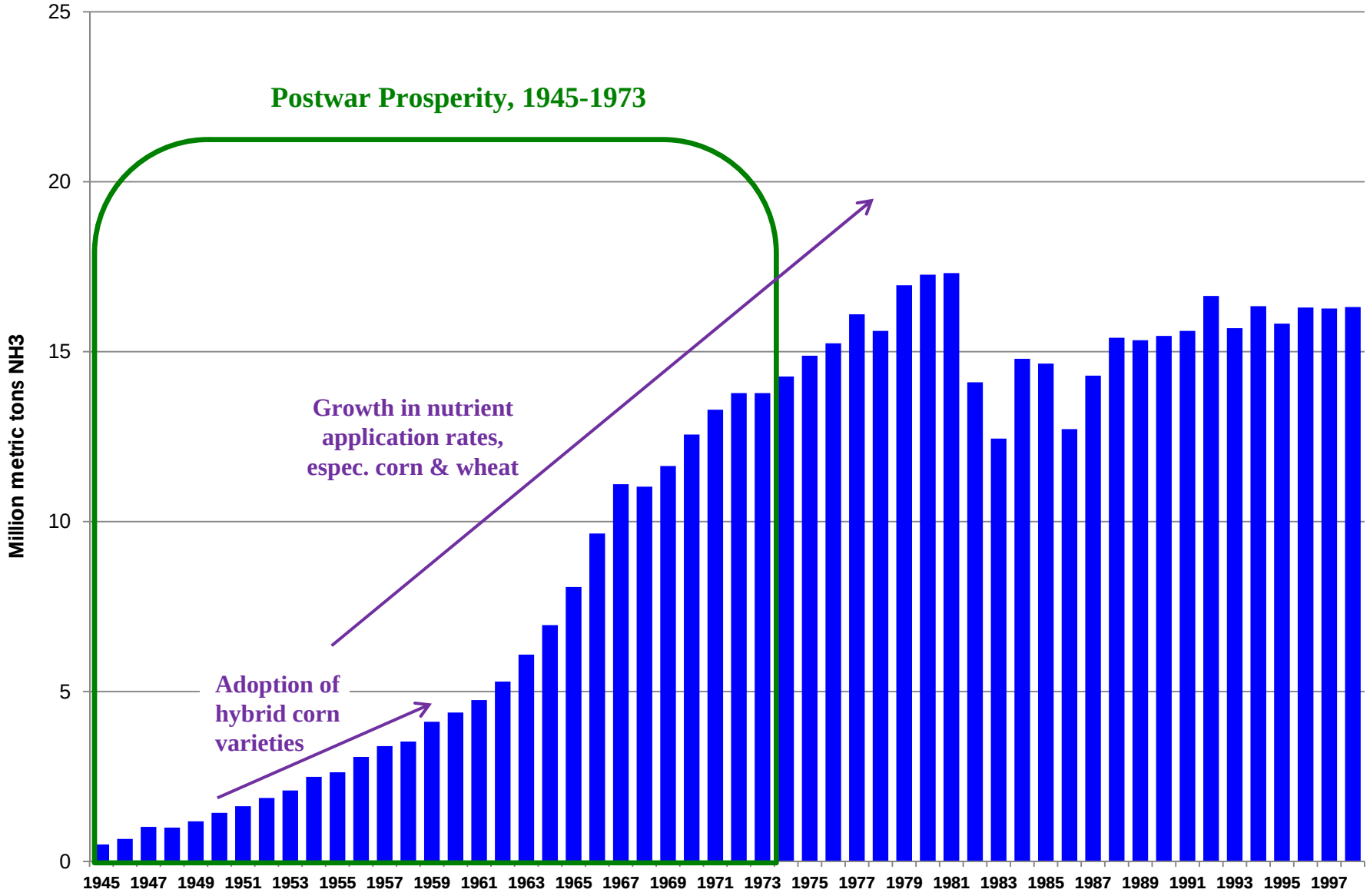
Sources: Nelson, 1990; Data, U.S. Geological Survey.

# U.S. Ammonia Production, 1945-1998

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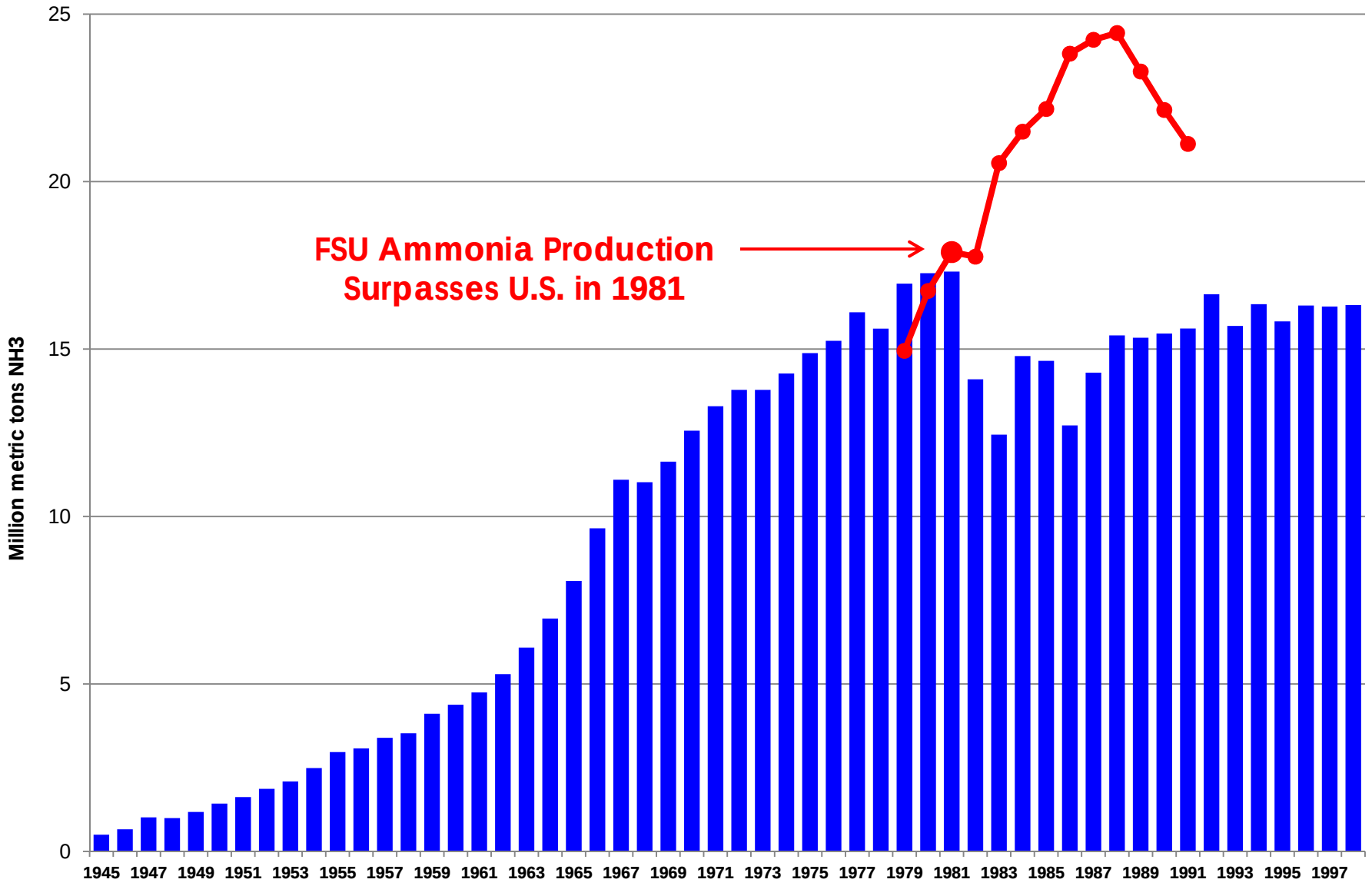
Source: U.S. Geological Survey, IFA, TFI.

# U.S. Ammonia Production, 1945-1998

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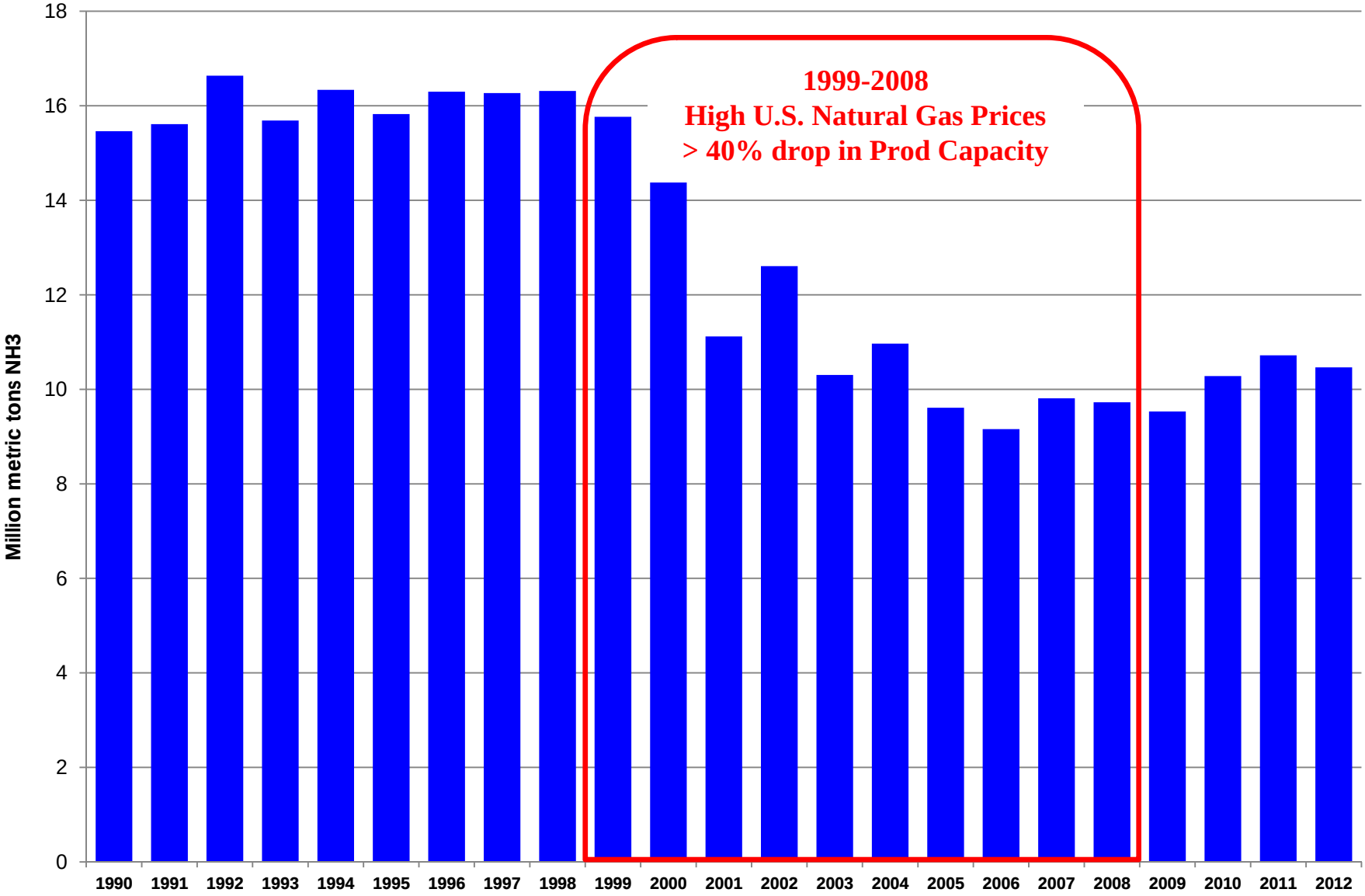
Source: U.S. Geological Survey, IFA, TFI.

# U.S. Ammonia Production

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Source: TFI, IFA.

# CHINA

隨著食品在手，你安心

“With food in hand, you have peace of mind”

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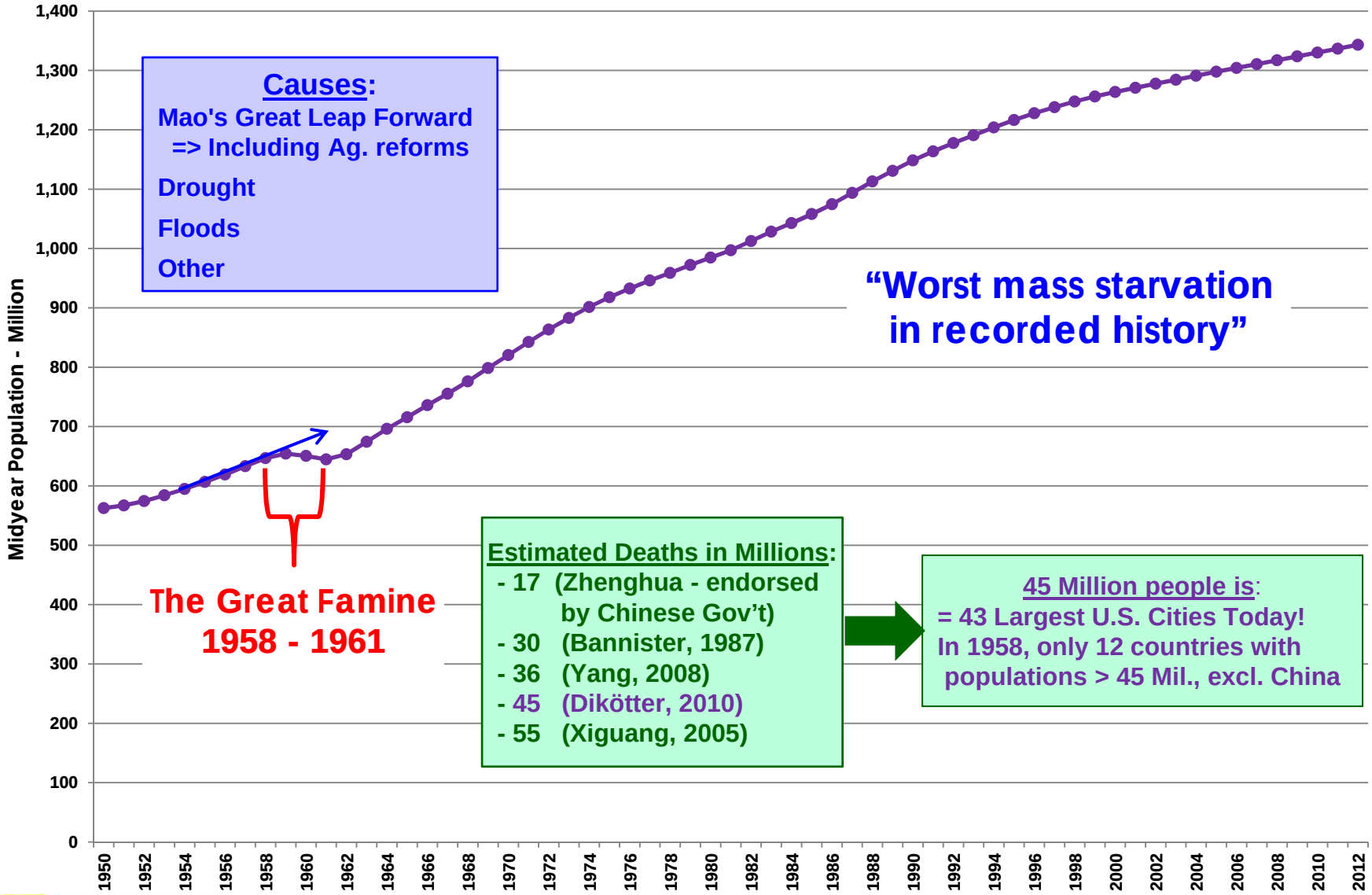
# China – The Great Famine

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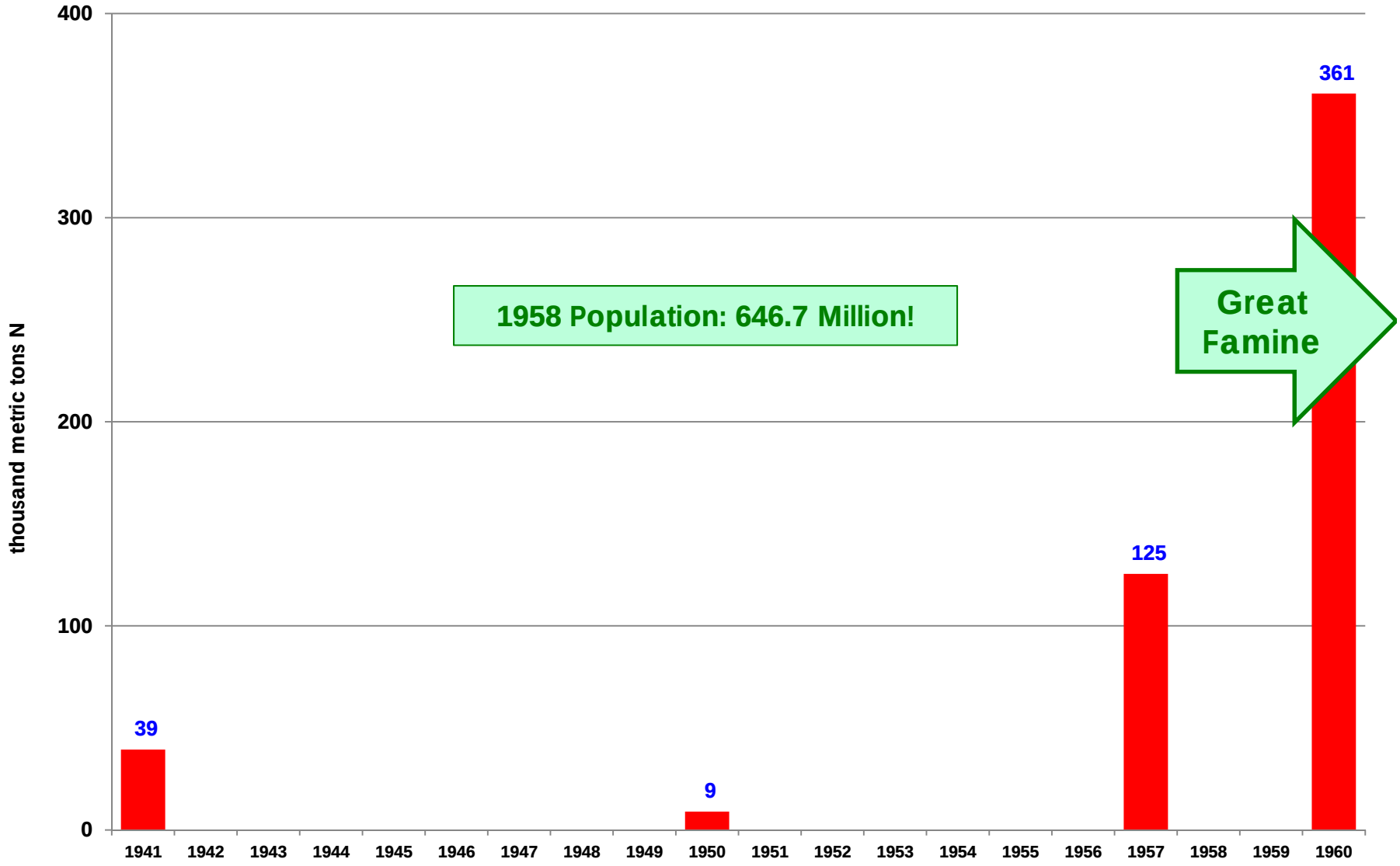
Source: Tombstone, Yang Jinsheng, 2008; Mao's Great Famine, Frank Dikötter, 2010; U.S. Census Bureau.

# China Ammonia Production, 1941-1960

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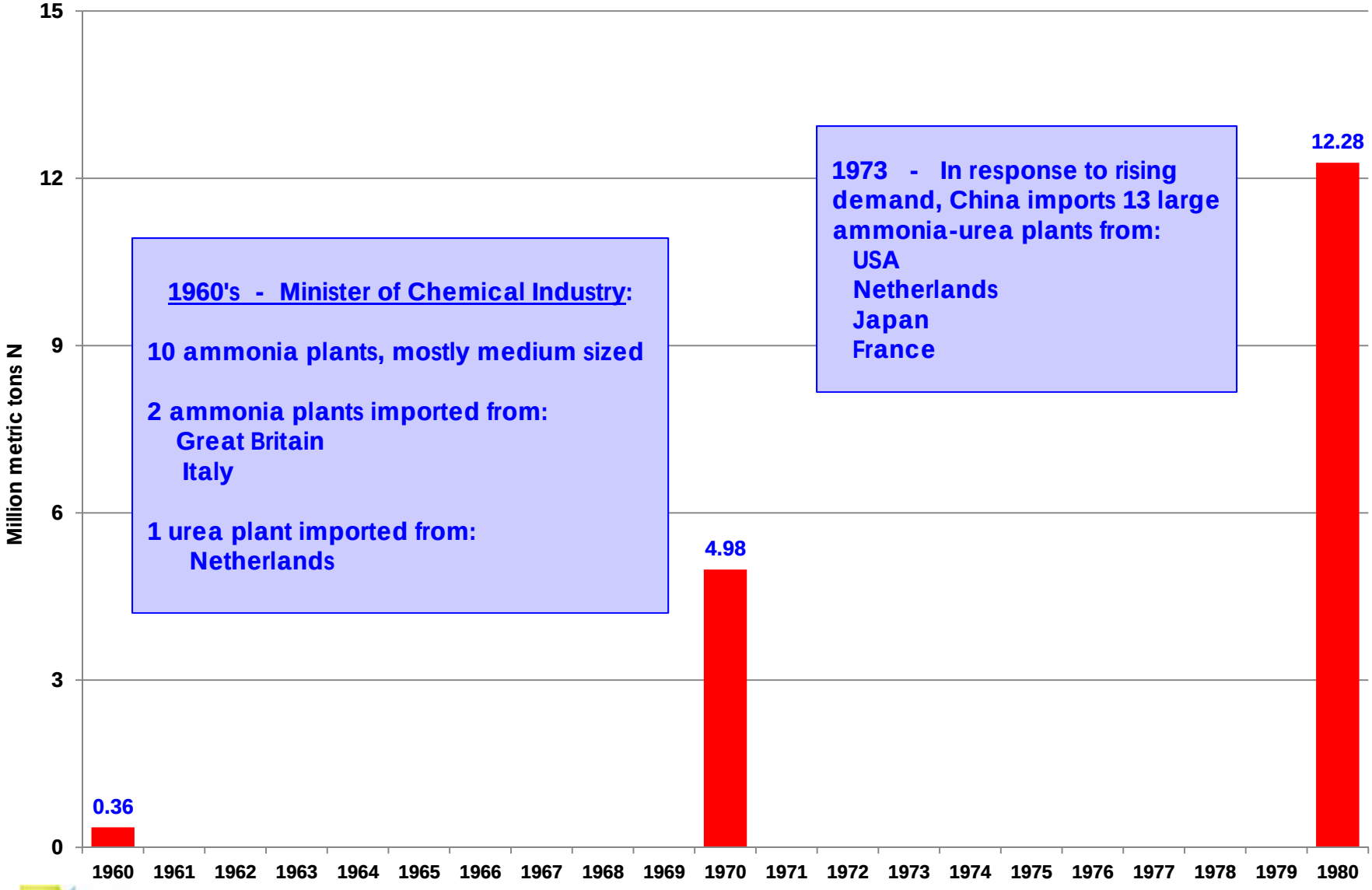
Data Source: 1941 and 1957, Dong Gaojie, 1989; 1950 and 1960, Long Xingmao, 1987.

# China Ammonia Production, 1960-1980

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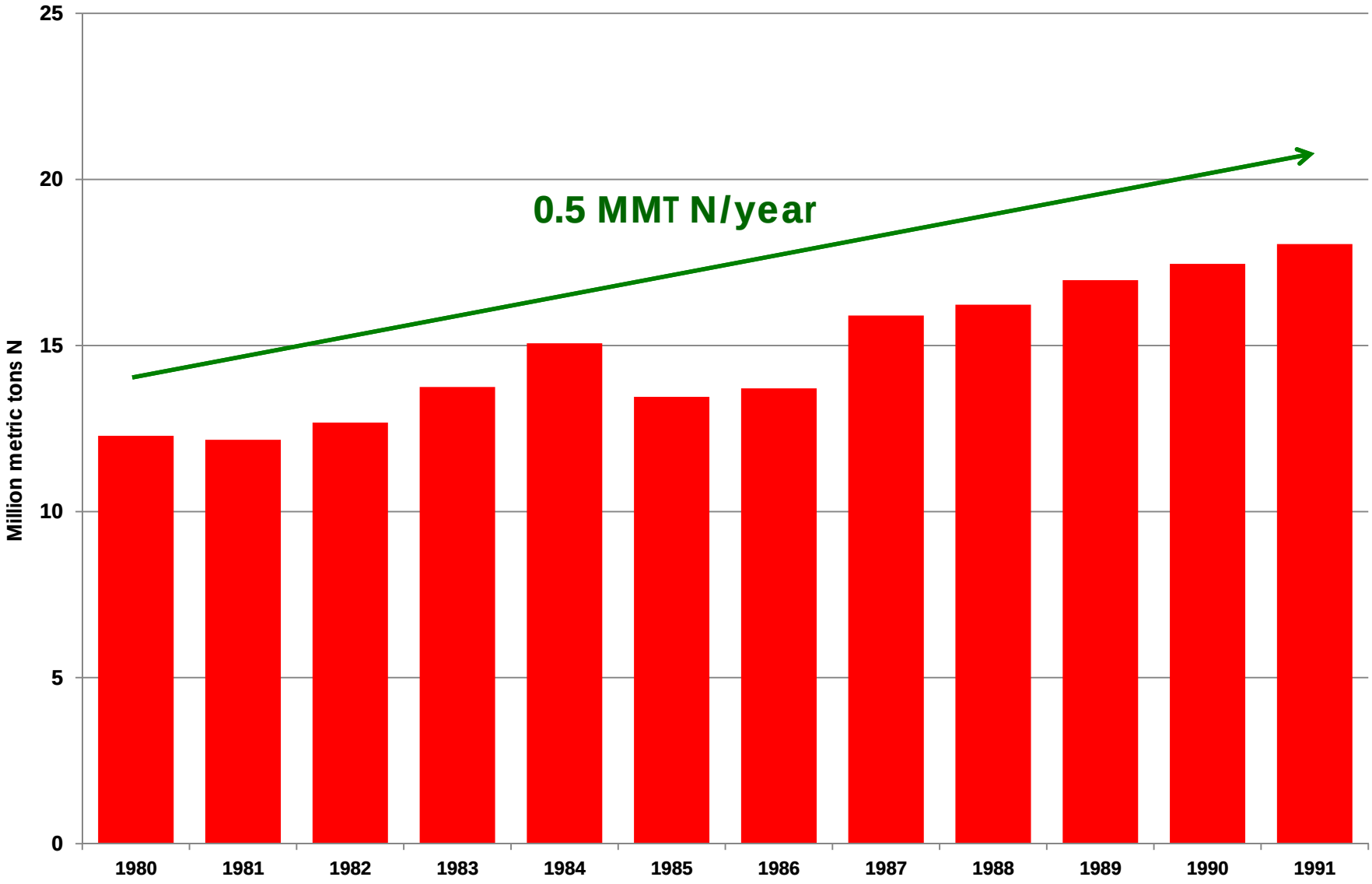
Source: Data: Huang Gaoqiang, Beijing University; Information - The Chemical Fertilizer Industry in China: A Review and its Outlook, Wang, Wang, Mai, et al, IFA, 2009.

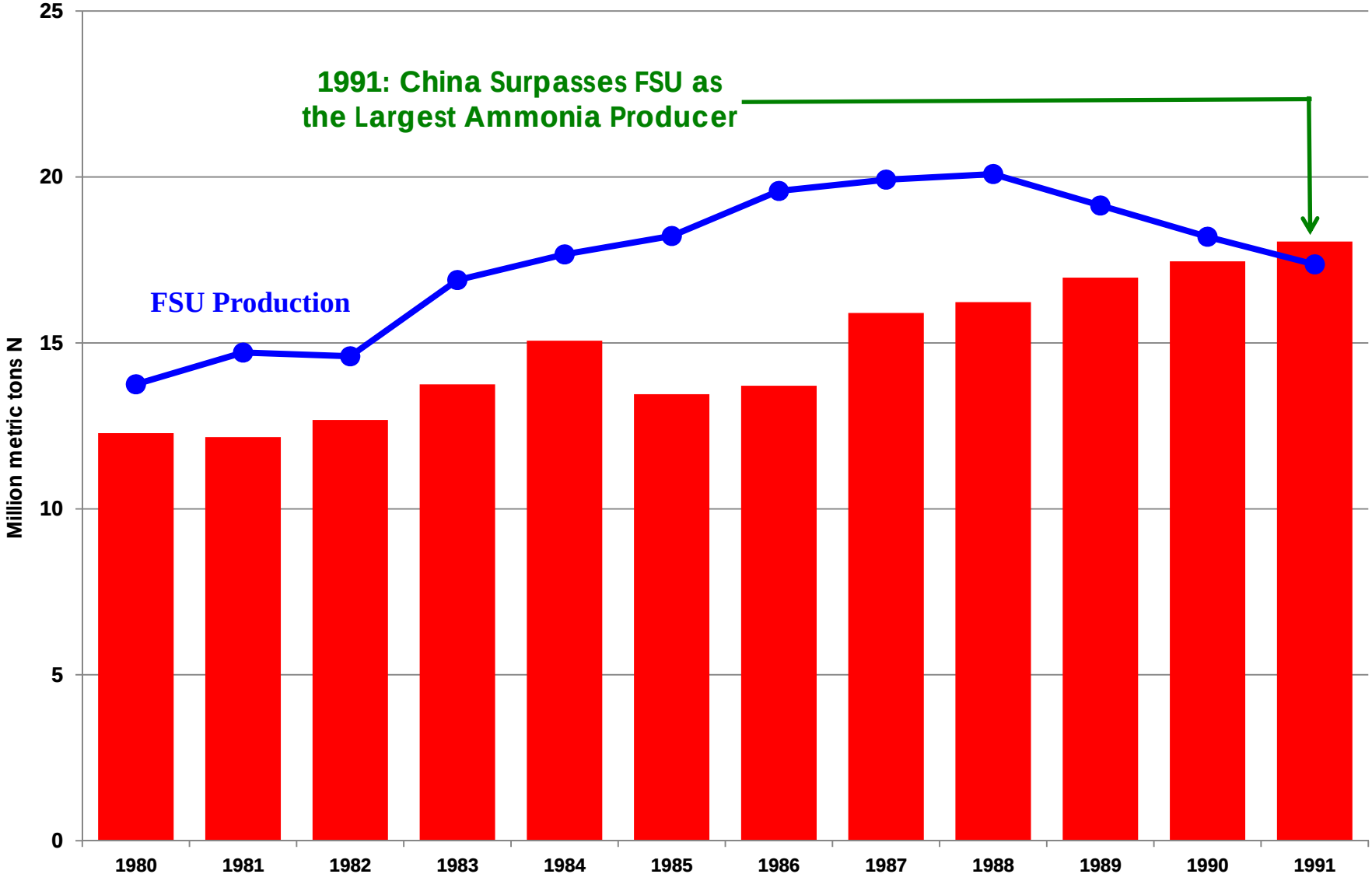
# China Ammonia Production, 1980-1991




The Fertilizer Institute

Data Source: IFA.

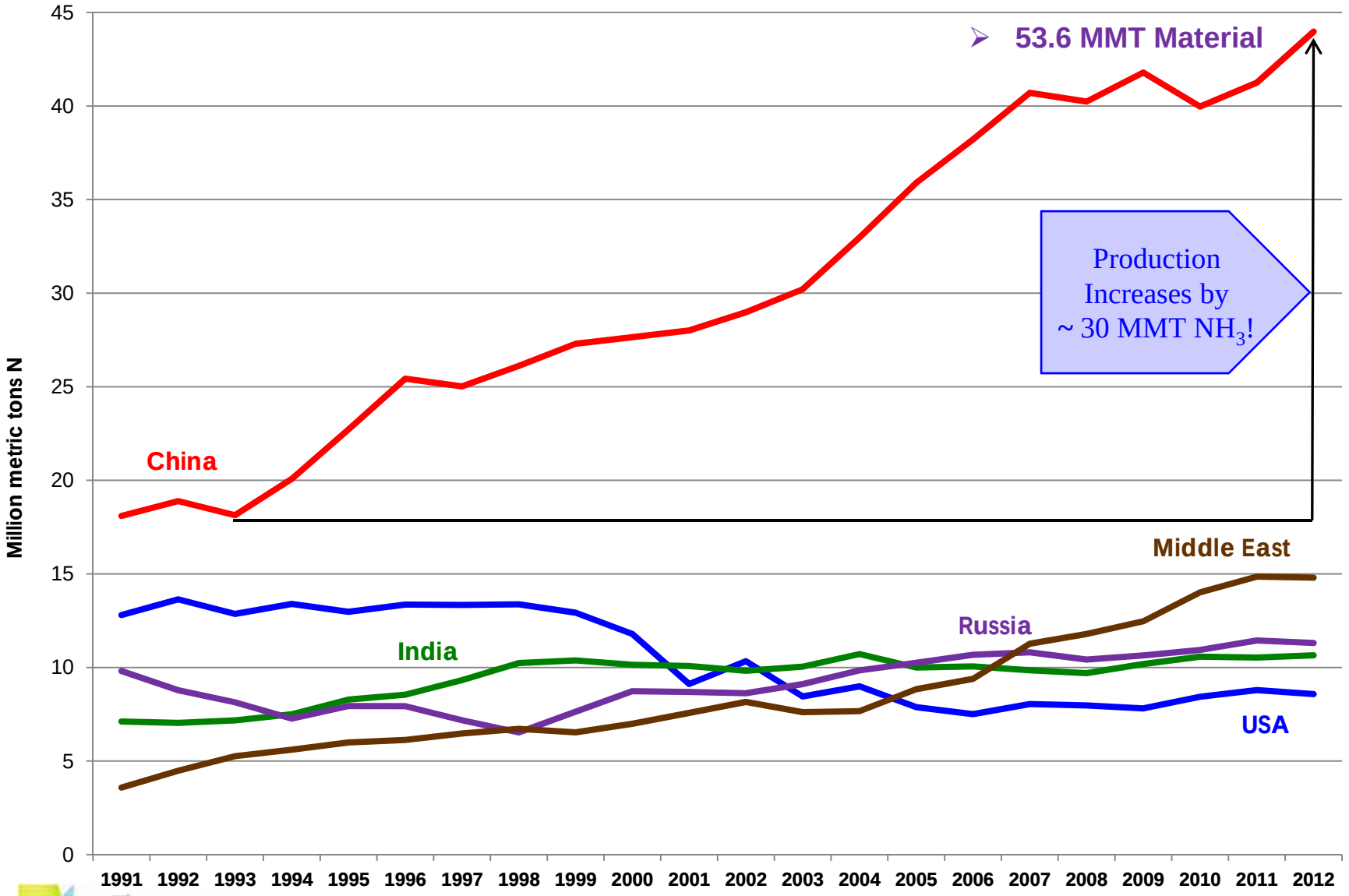
# China Ammonia Production, 1980-1991




The Fertilizer Institute

Data Source: IFA.

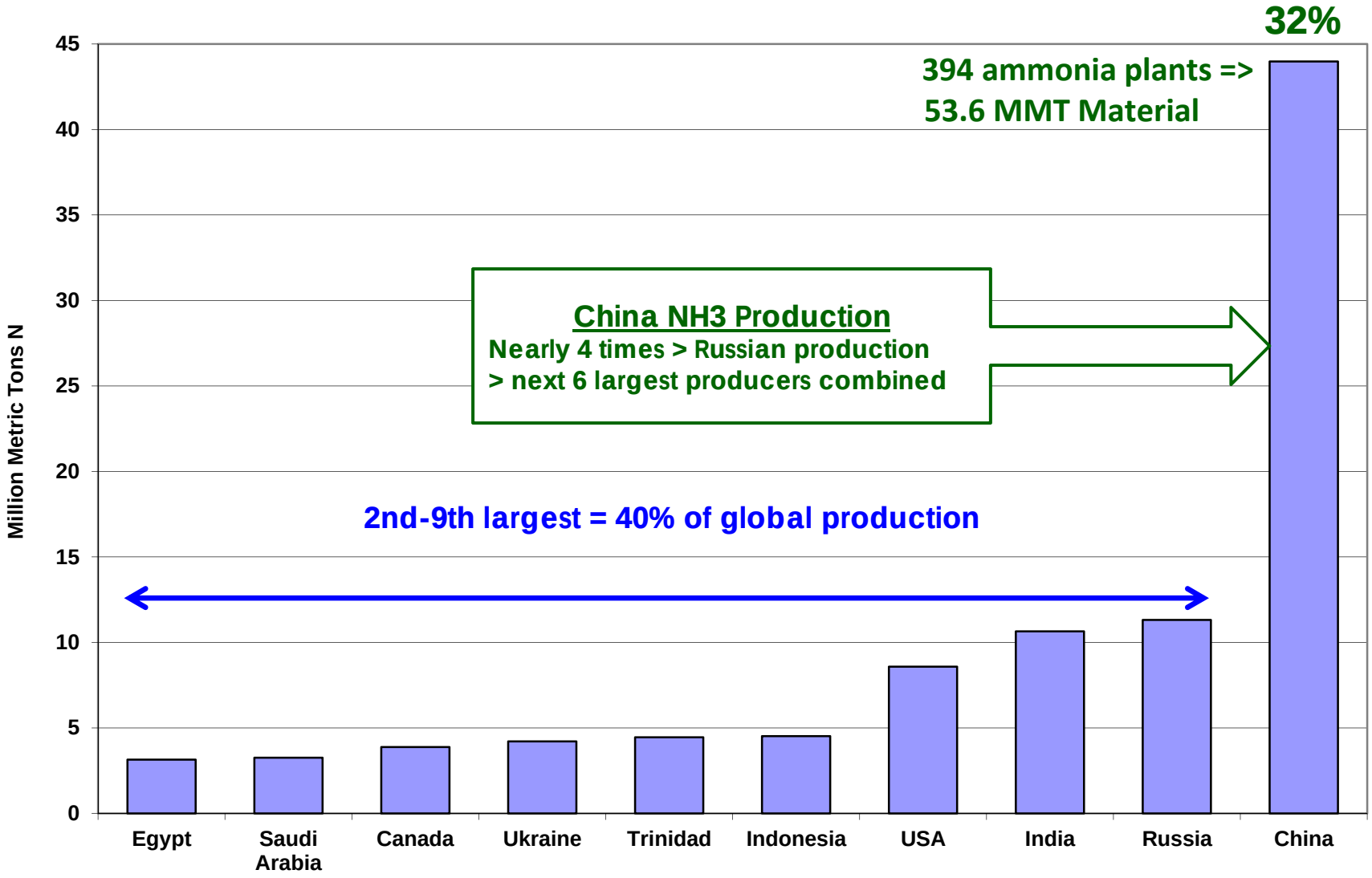
# Largest Ammonia Producing Countries




The Fertilizer Institute

Data Source: IFA.

# Top 10 Ammonia Producing Countries in 2012

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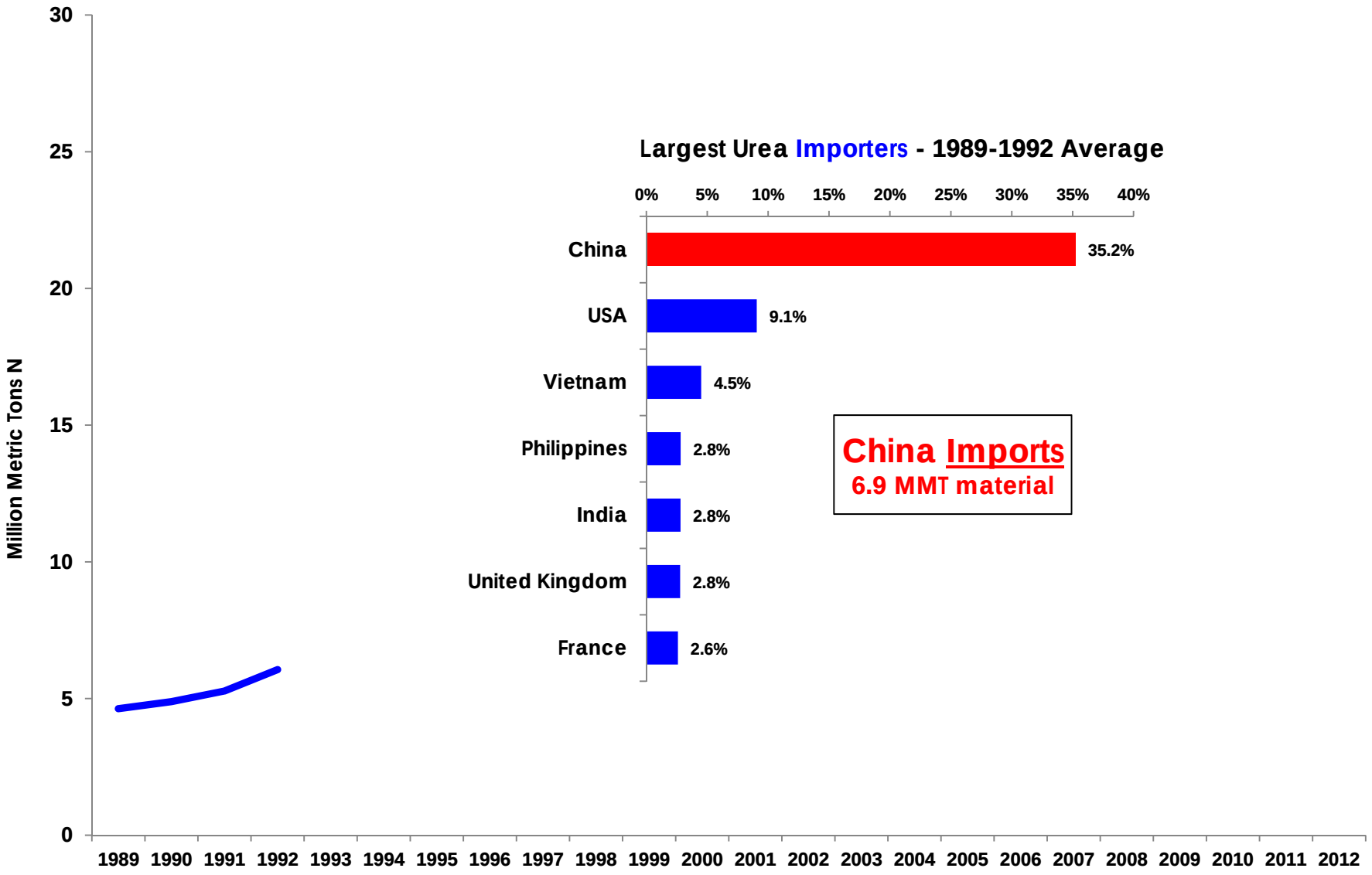
Source: Data - IFA; No. of ammonia plants - Zhang and Huang, 2013 IFA PIT Conference, Oct. 2013.

# China - Urea Production

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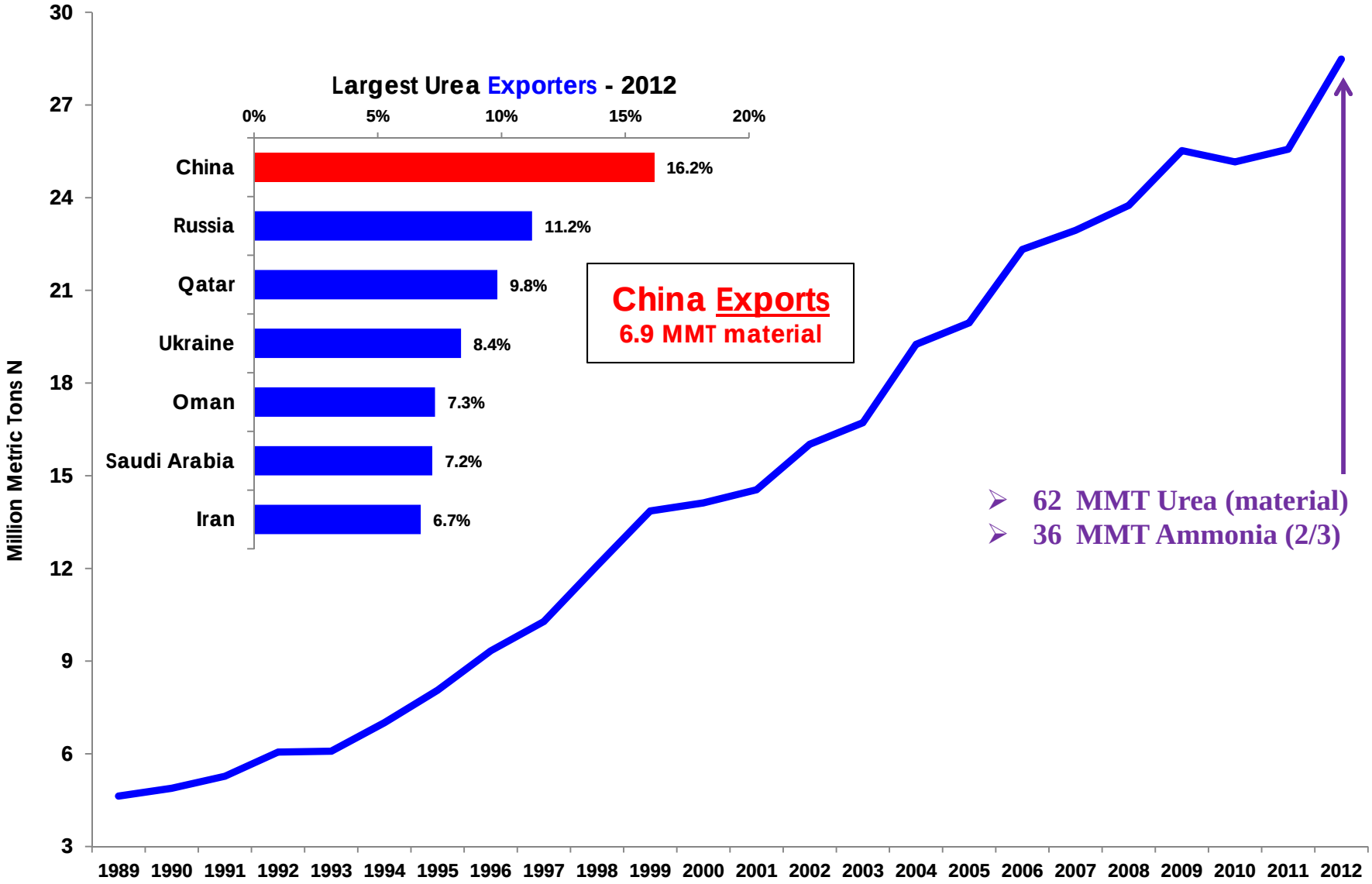
Data Source: IFA.

# China - Urea Production

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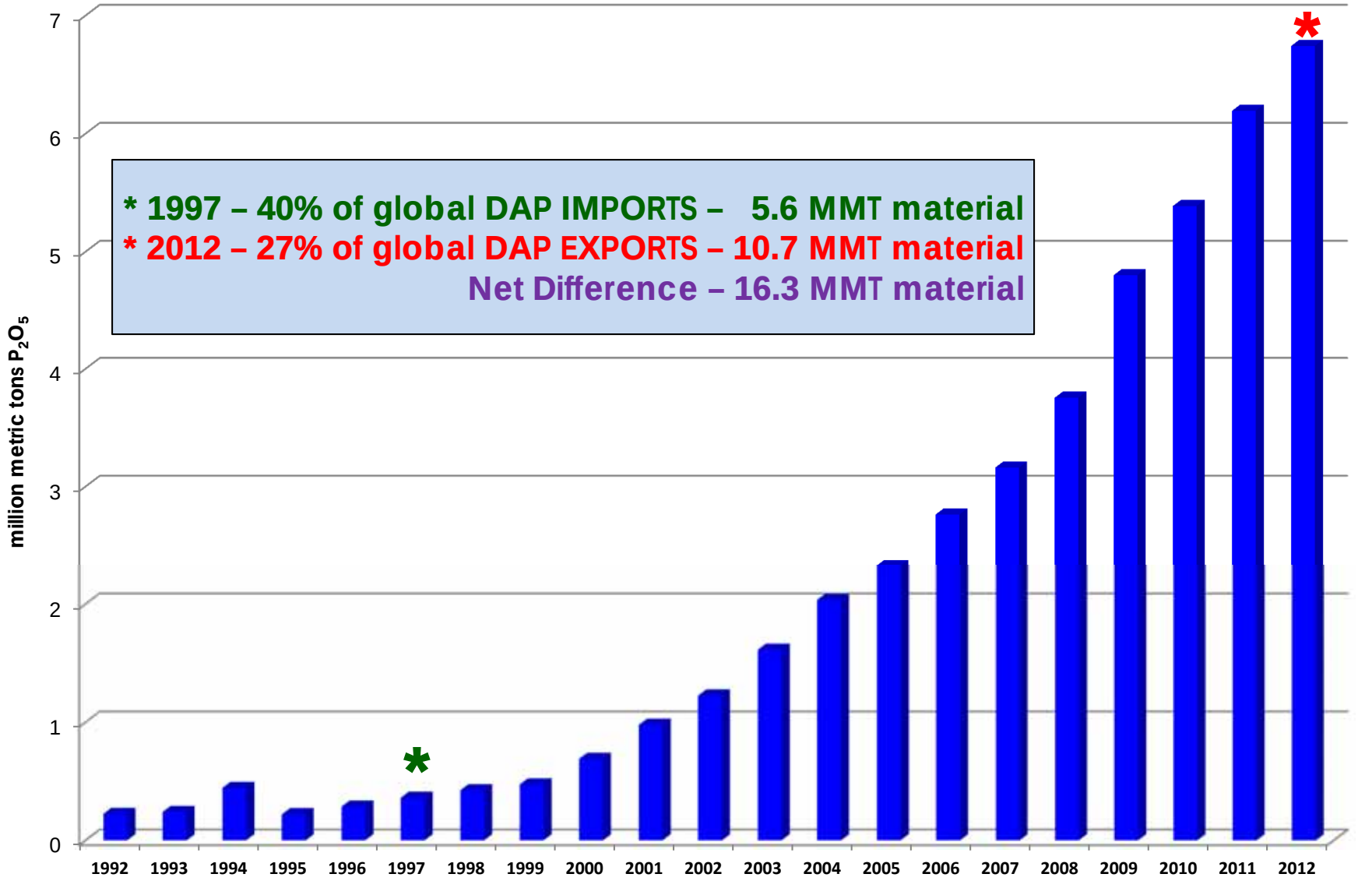
Data Source: IFA.

# China: DAP Production

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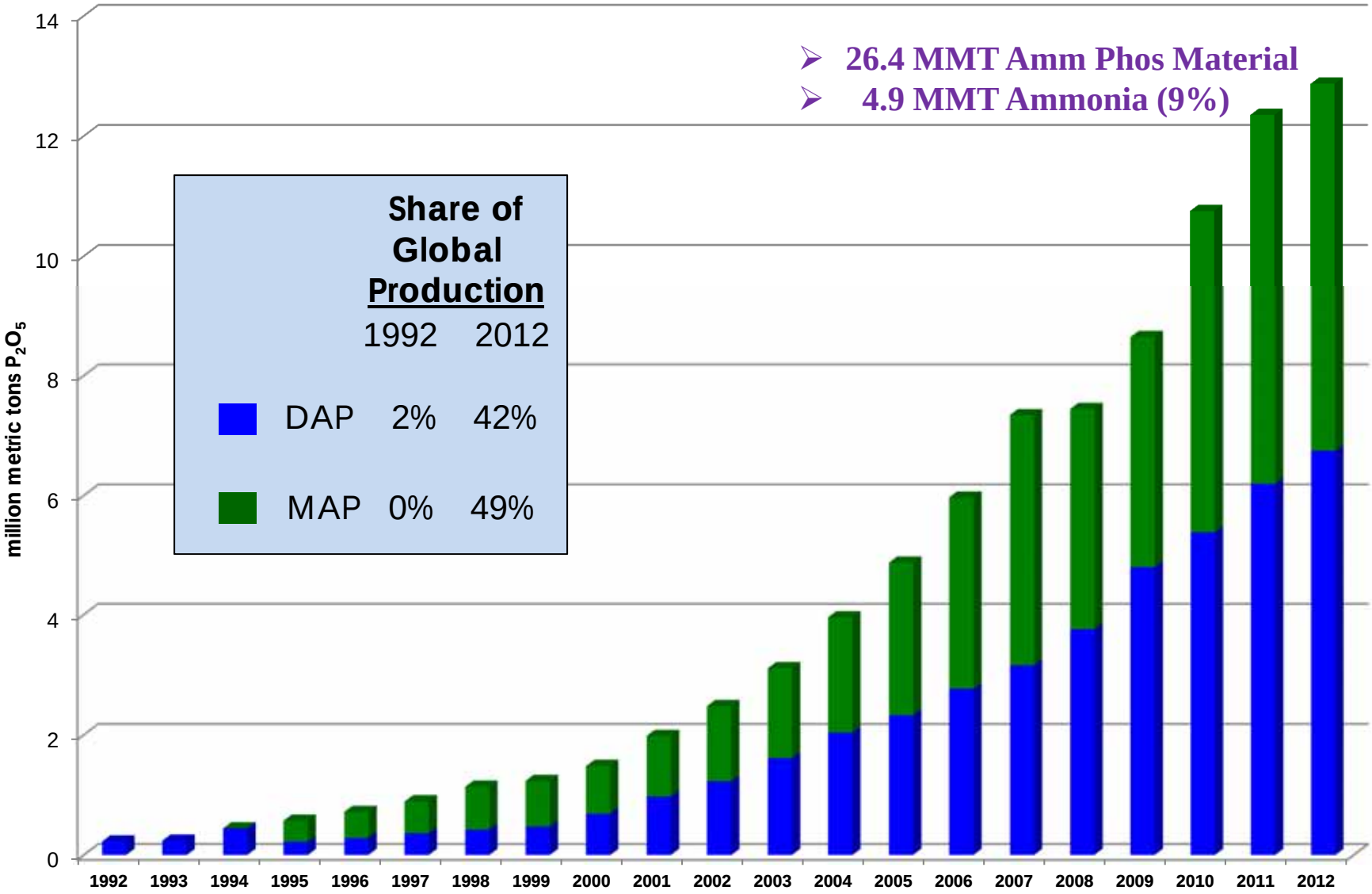
Data Source: IFA.

# China: Phosphate Fertilizer Production

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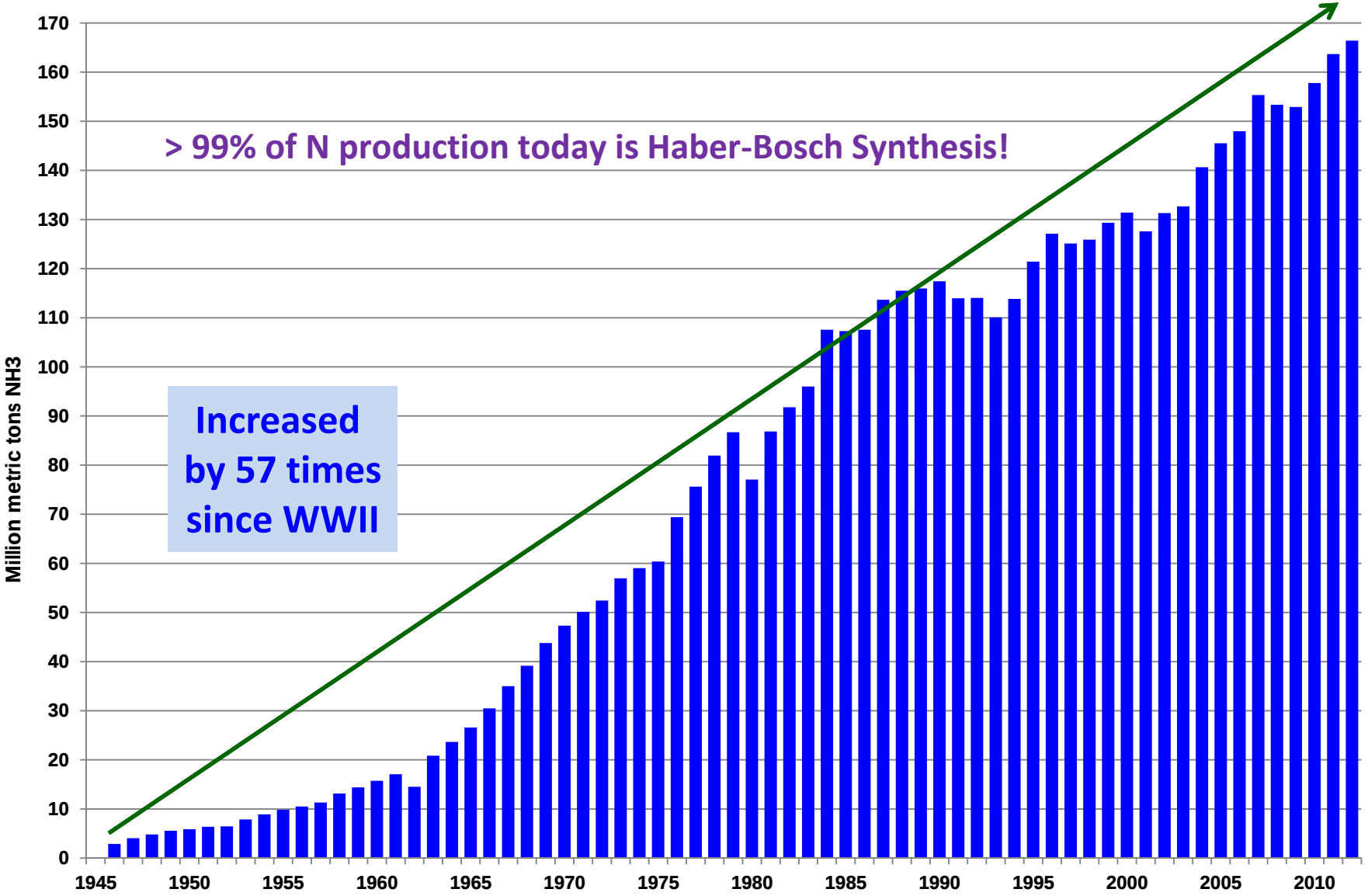
Data Source: IFA.

# Global Ammonia Production

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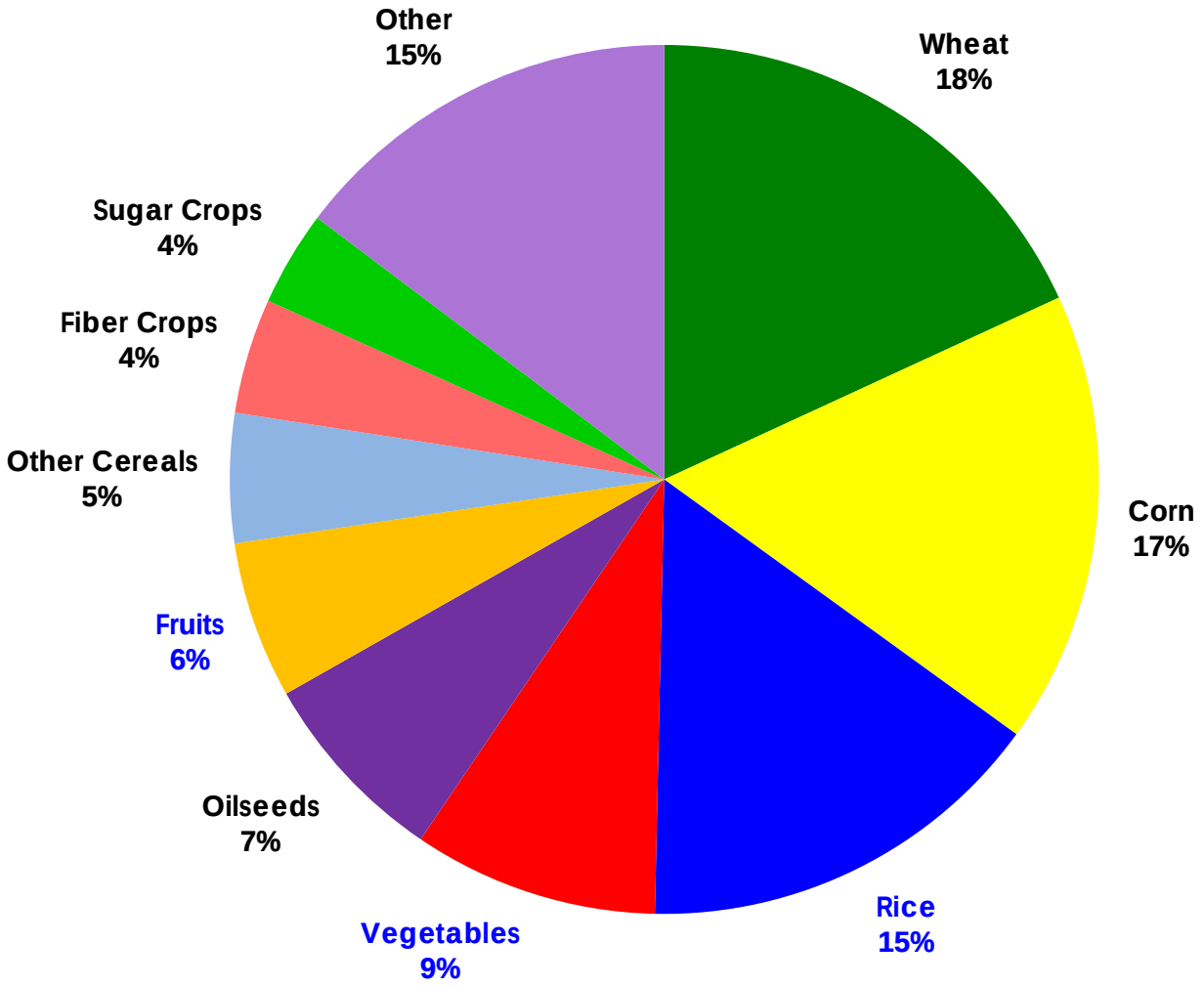
Source: 1943-1979: U.S. Geological Survey; 1980-2012: IFA; Smil, 2001.

# Global Nitrogen Use by Crop, 2010/11

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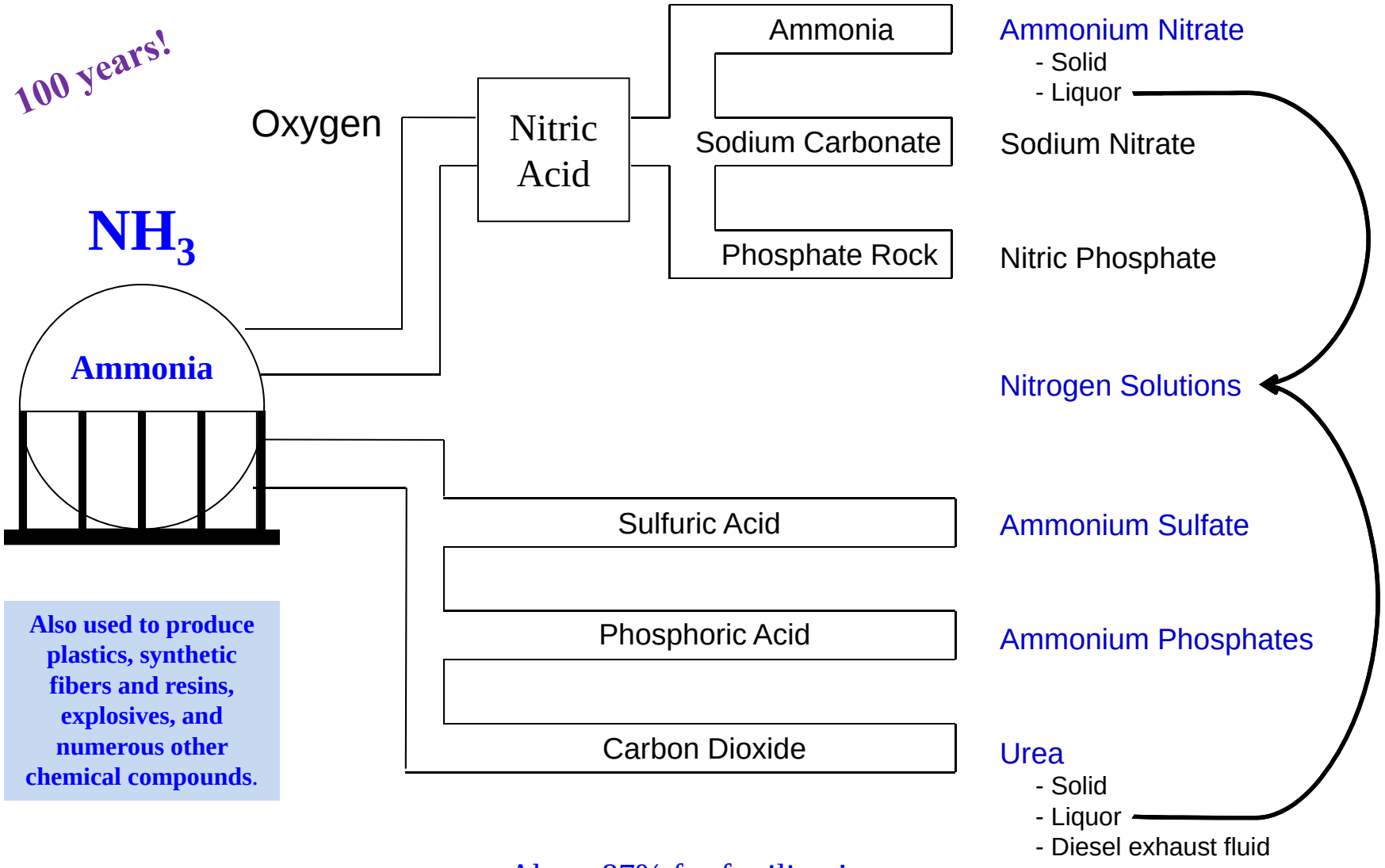
Source: IFA.

# "Downstream" Nitrogen Fertilizers and Materials from Anhydrous Ammonia




About 87% for fertilizer!

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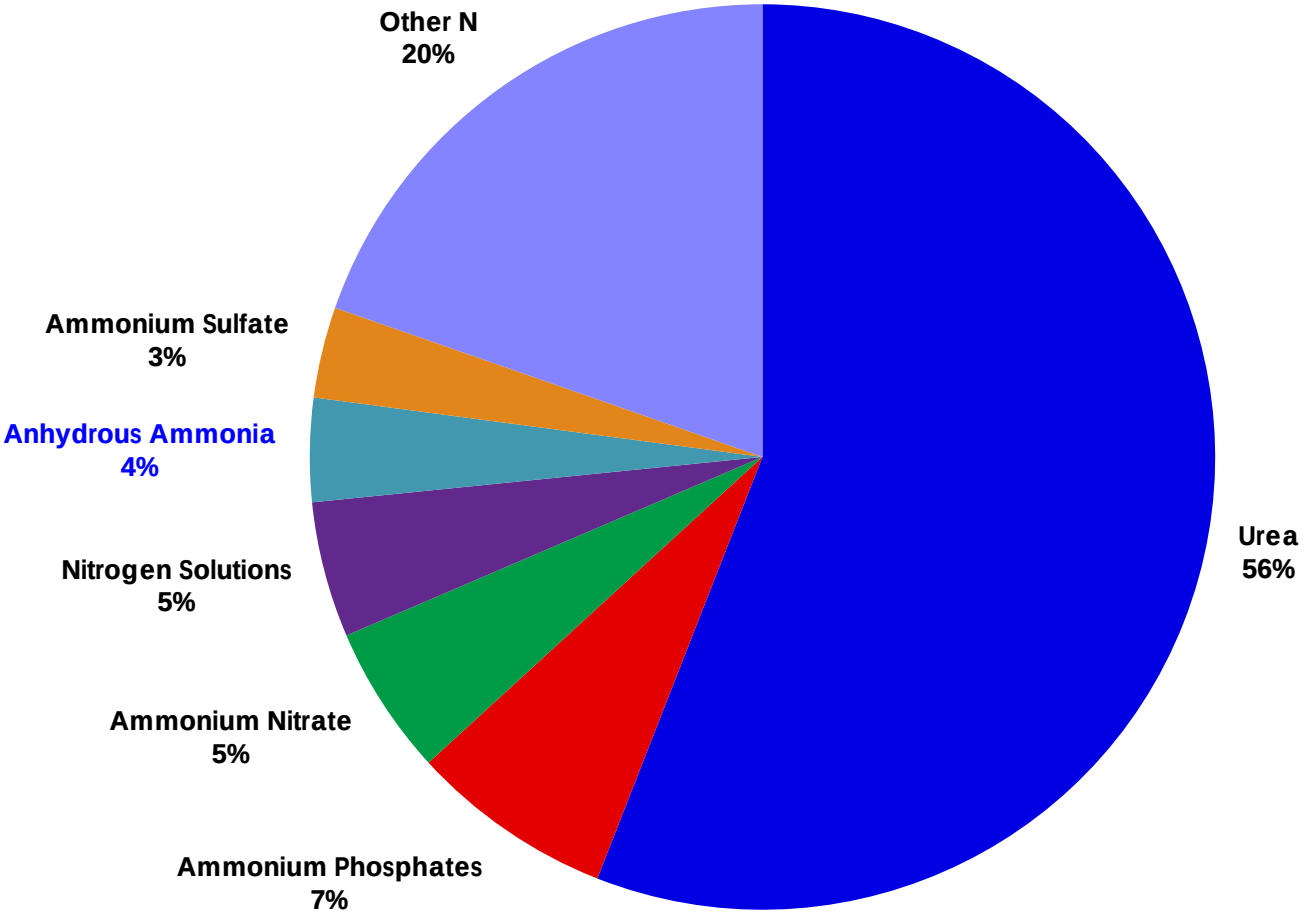
# World Nitrogen Fertilizer Use

## 2011 - 107.9 million metric tons N

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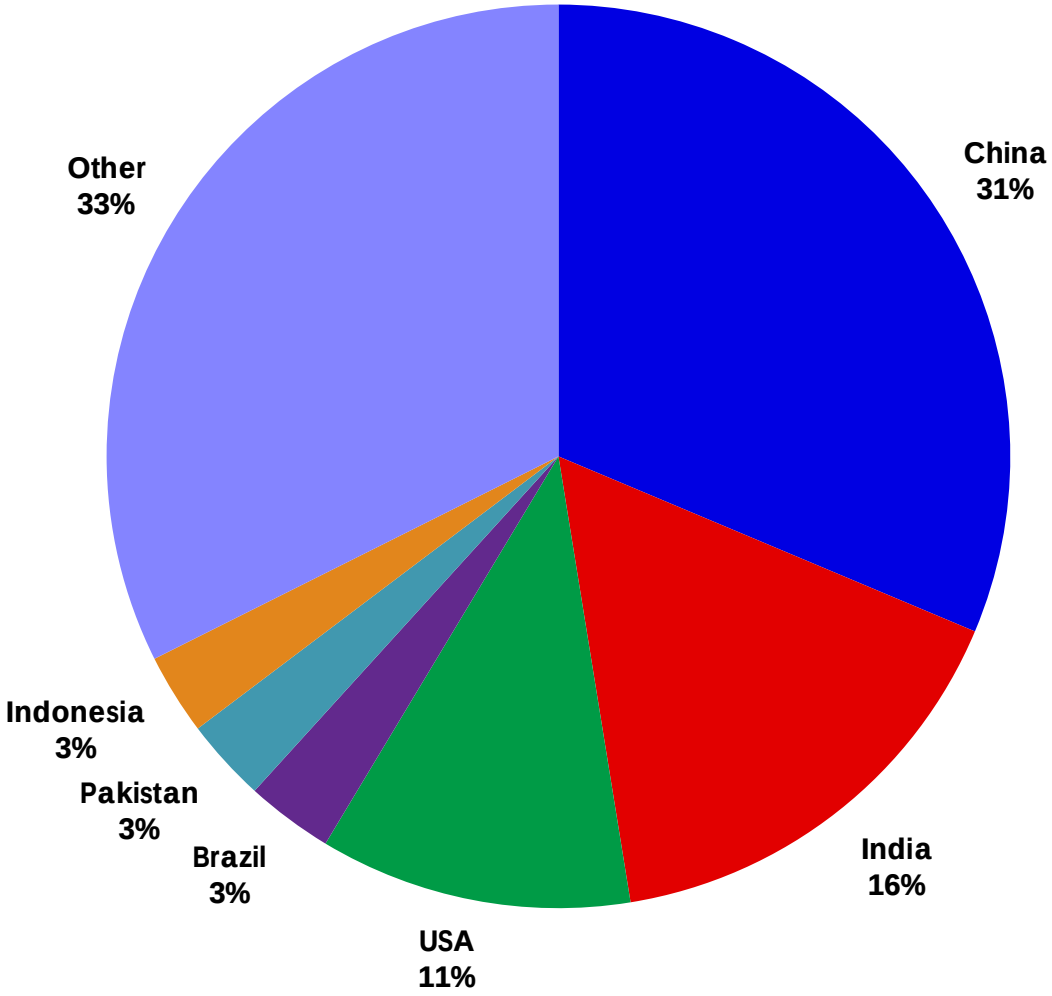
Source: IFA.

# World Nitrogen Fertilizer Use

## 2011 - 107.9 million metric tons N

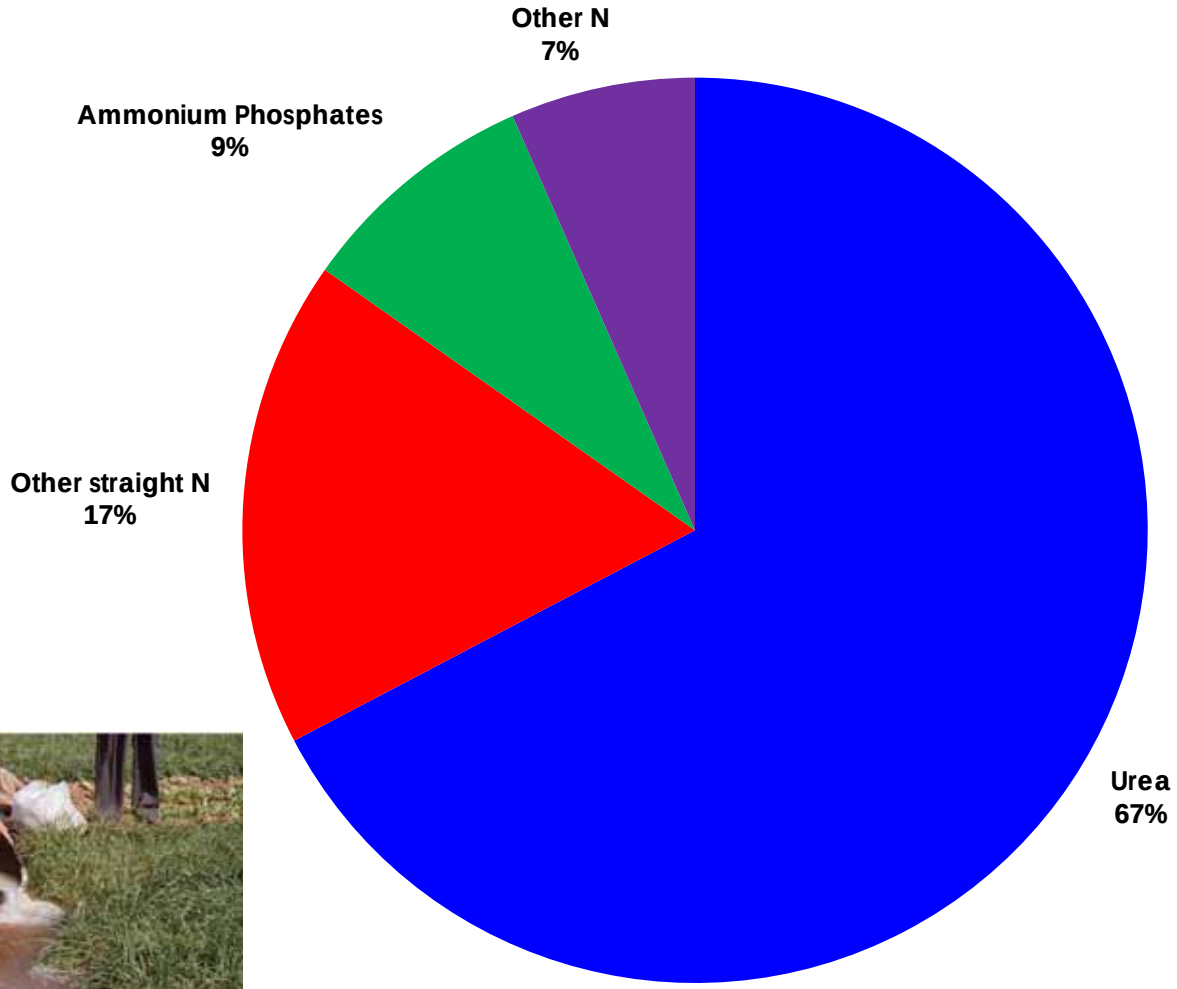



The Fertilizer Institute

Source: IFA.

# China - Nitrogen Fertilizer Use

## 2011 - 33.8 million metric tons N

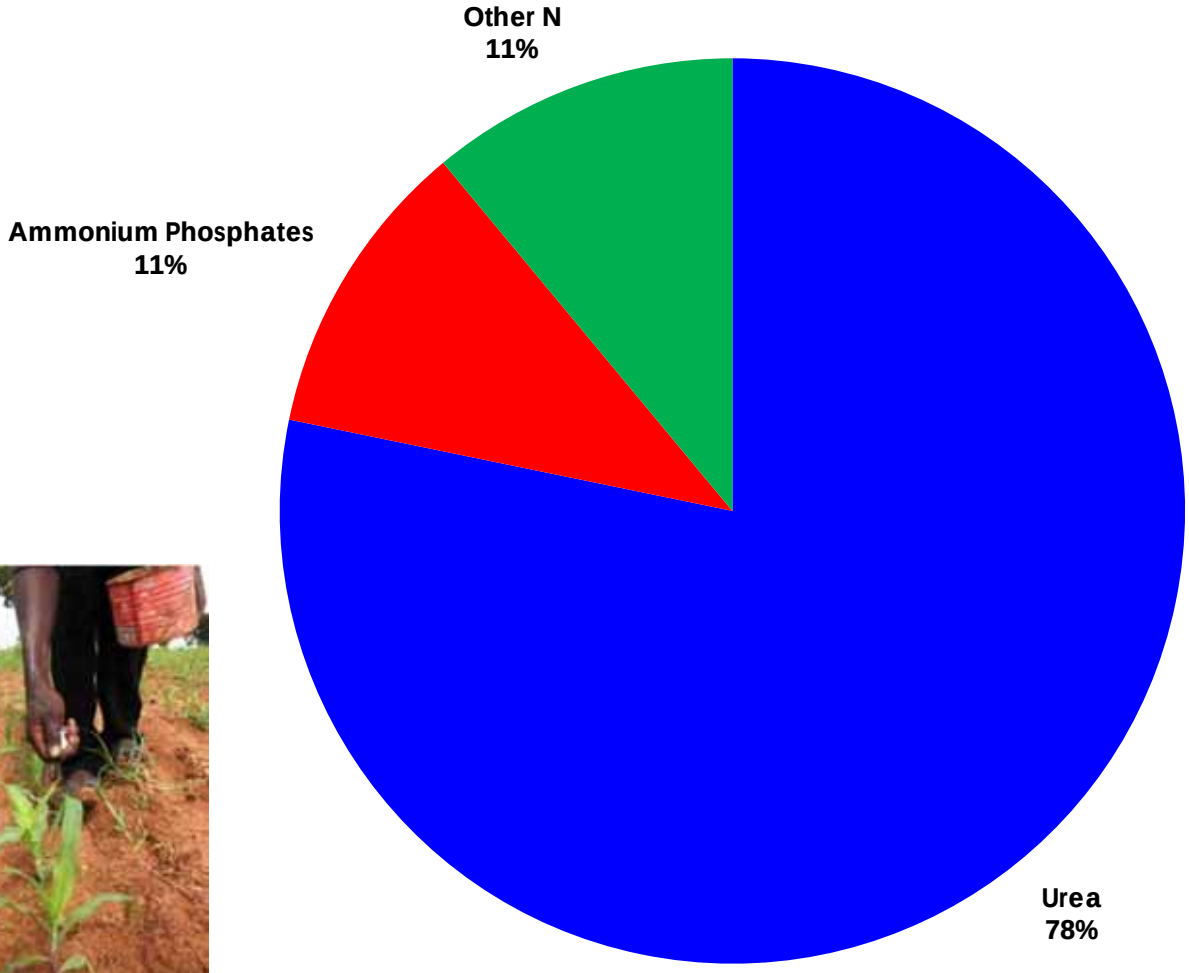



The Fertilizer Institute

Source: IFA.

# India - Nitrogen Fertilizer Use

## 2011 - 17.4 million metric tons N

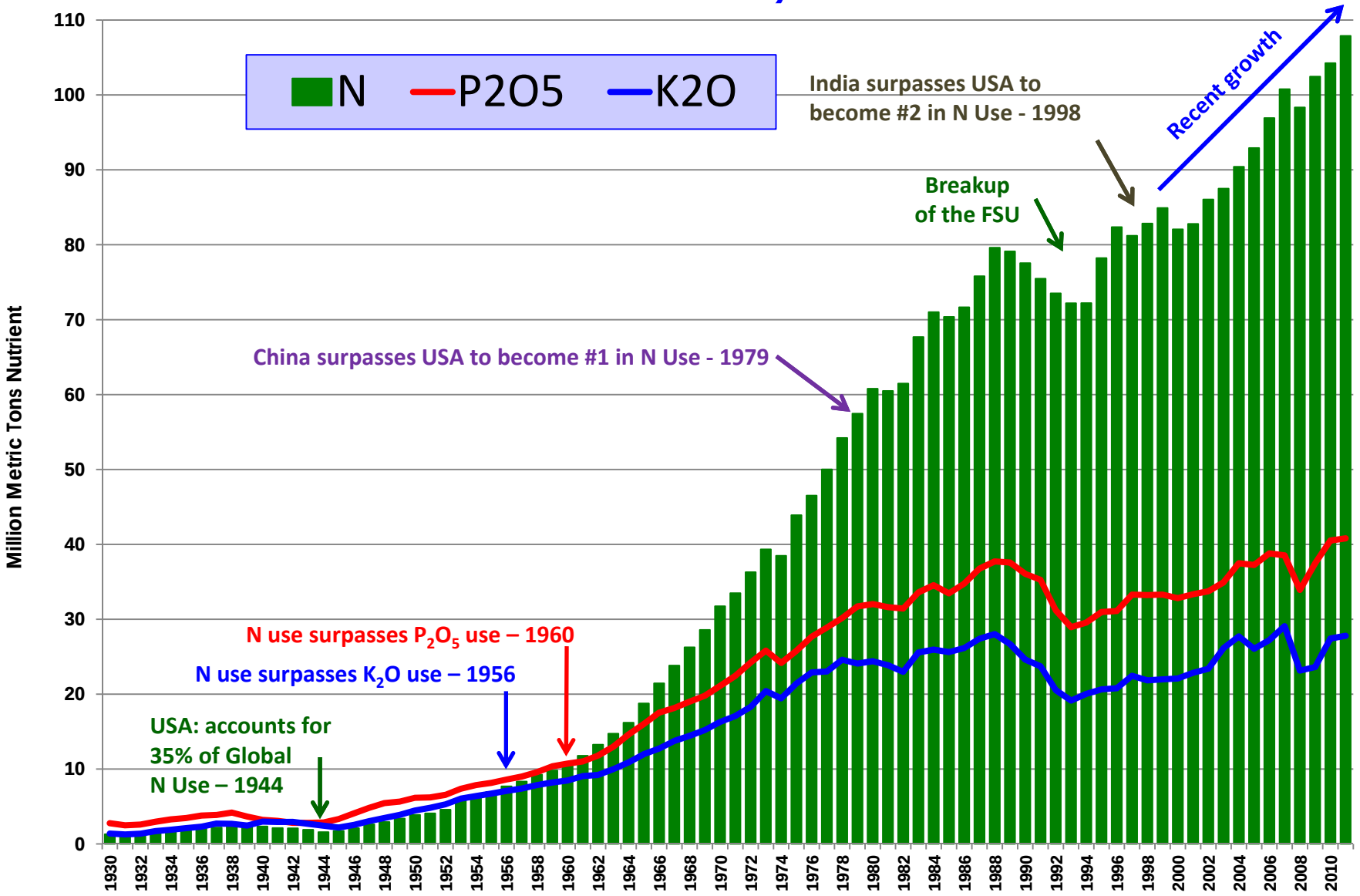





The Fertilizer Institute

Source: IFA.

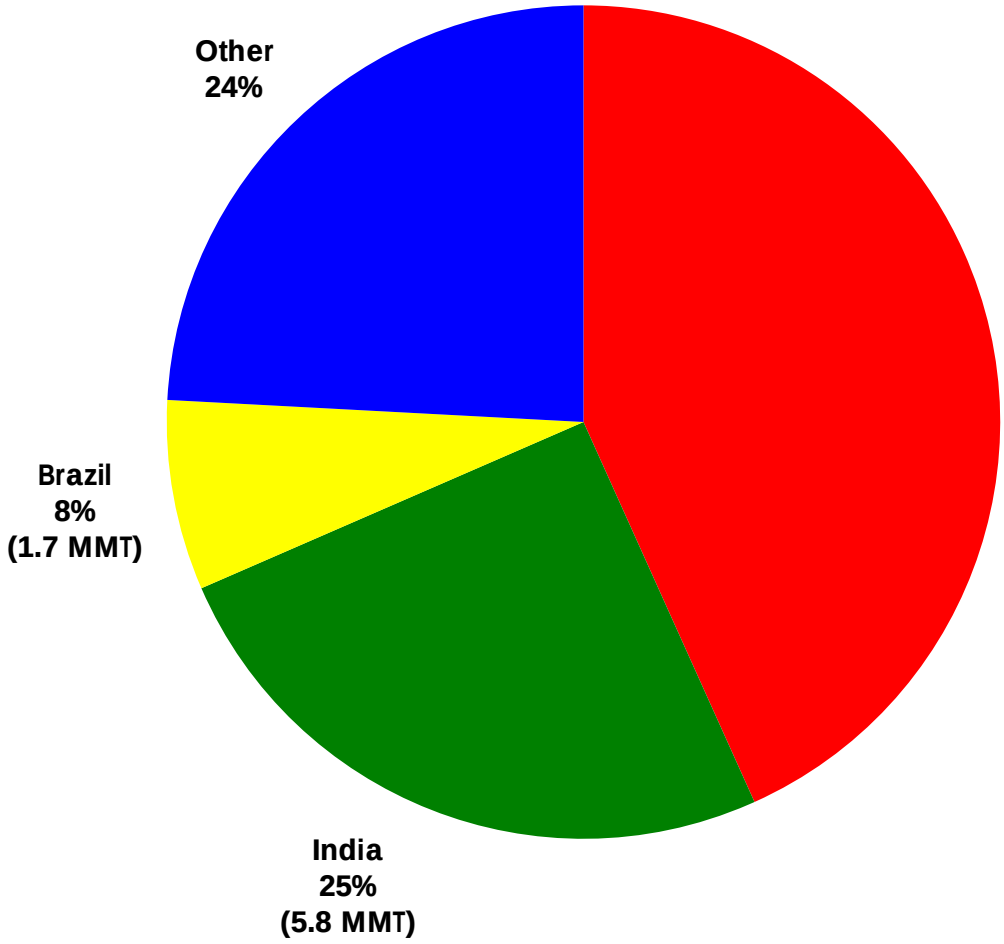
# Global Nutrient Use, 1930-2011




The Fertilizer Institute

Source: Data from IFA.

# Growth in Global Nitrogen Use
# 1999-2011: 23 MMT N

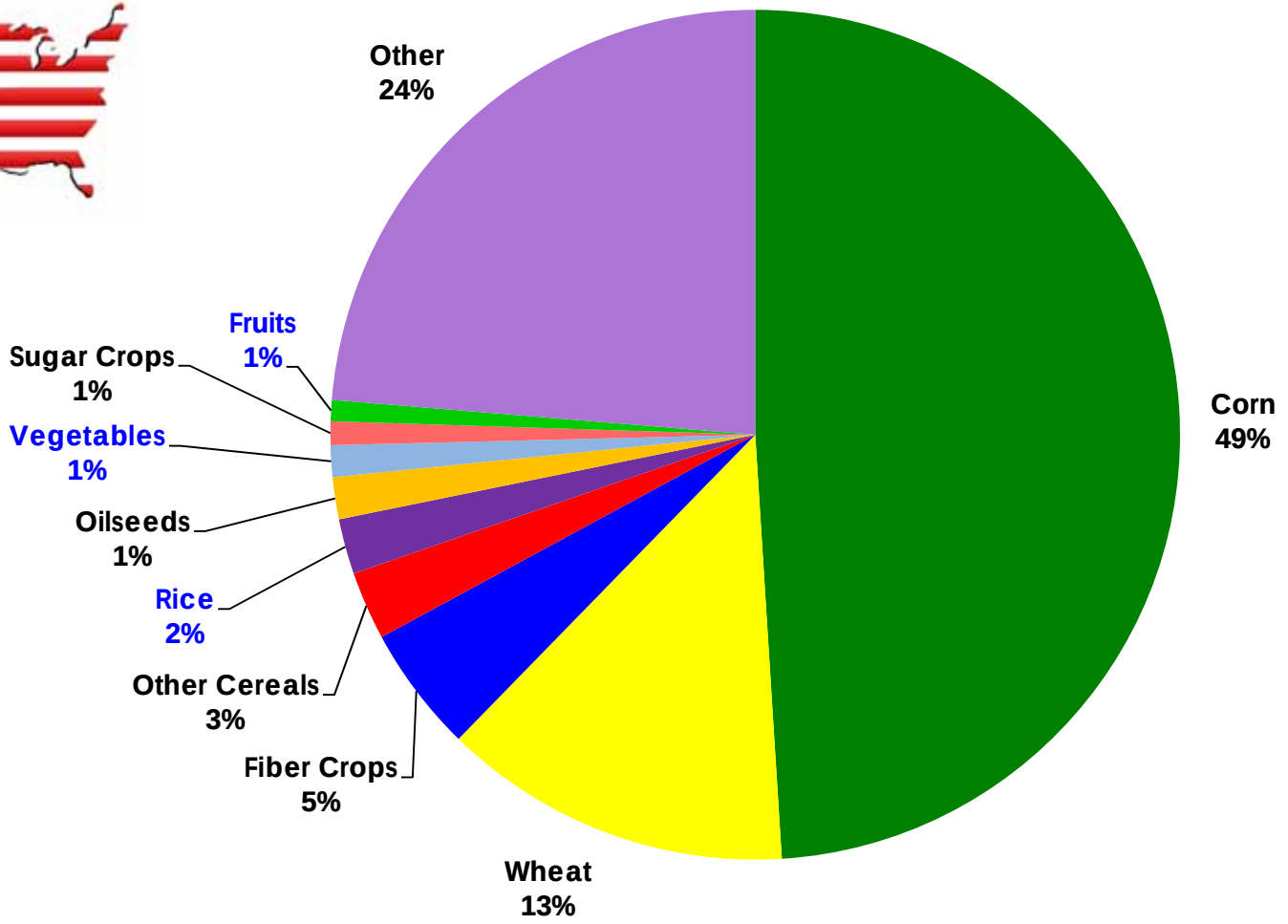



> 75%

The Fertilizer Institute

Source: IFA.

# U.S. Nitrogen Use by Crop, 2010/11

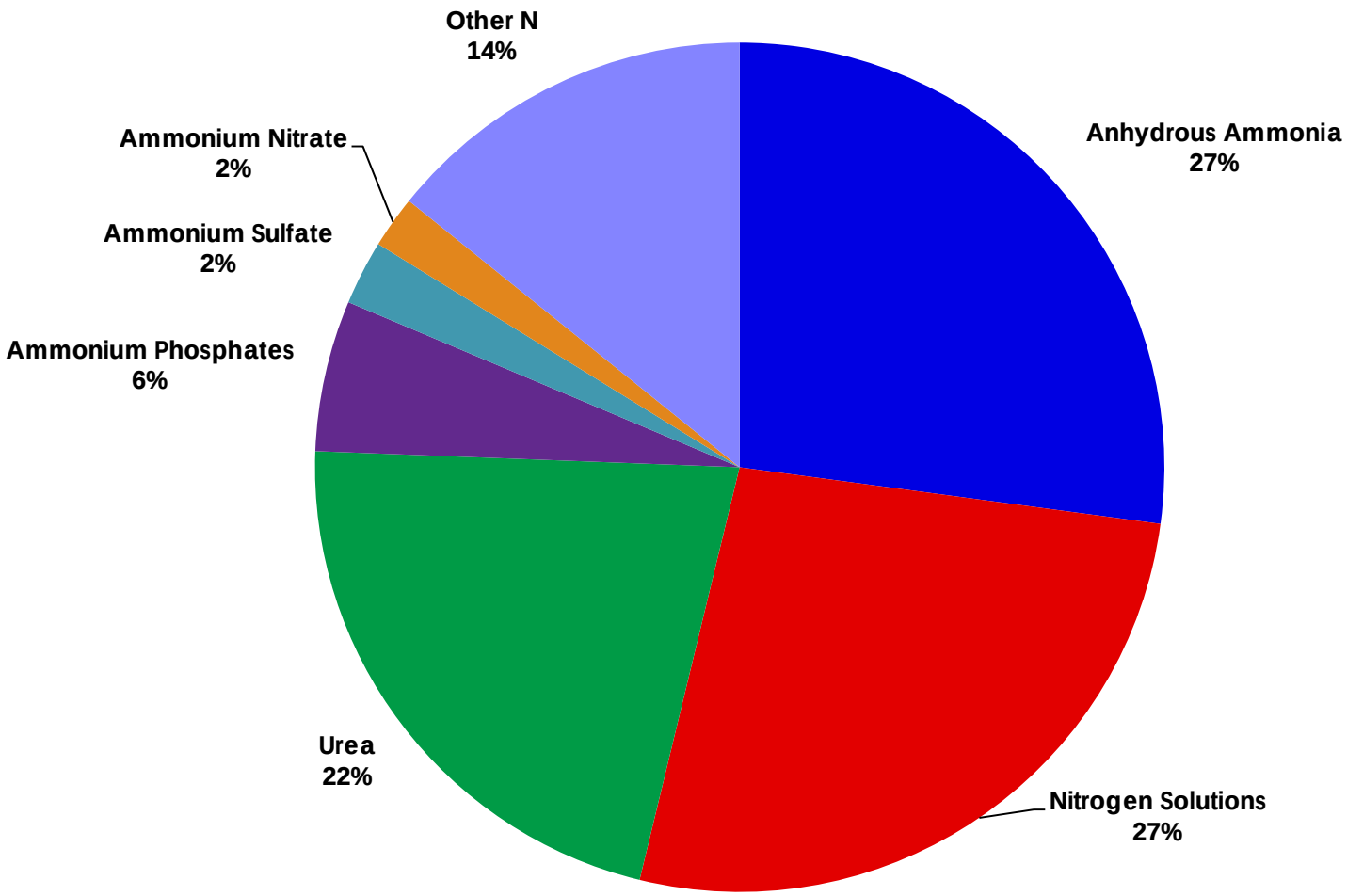



The Fertilizer Institute

Source: Computed from nutrient application rate data reported by USDA and Commercial Fertilizers, 2011.

# U.S. Nitrogen Fertilizer Use

## FY2010/11 - 12.84 million tons N



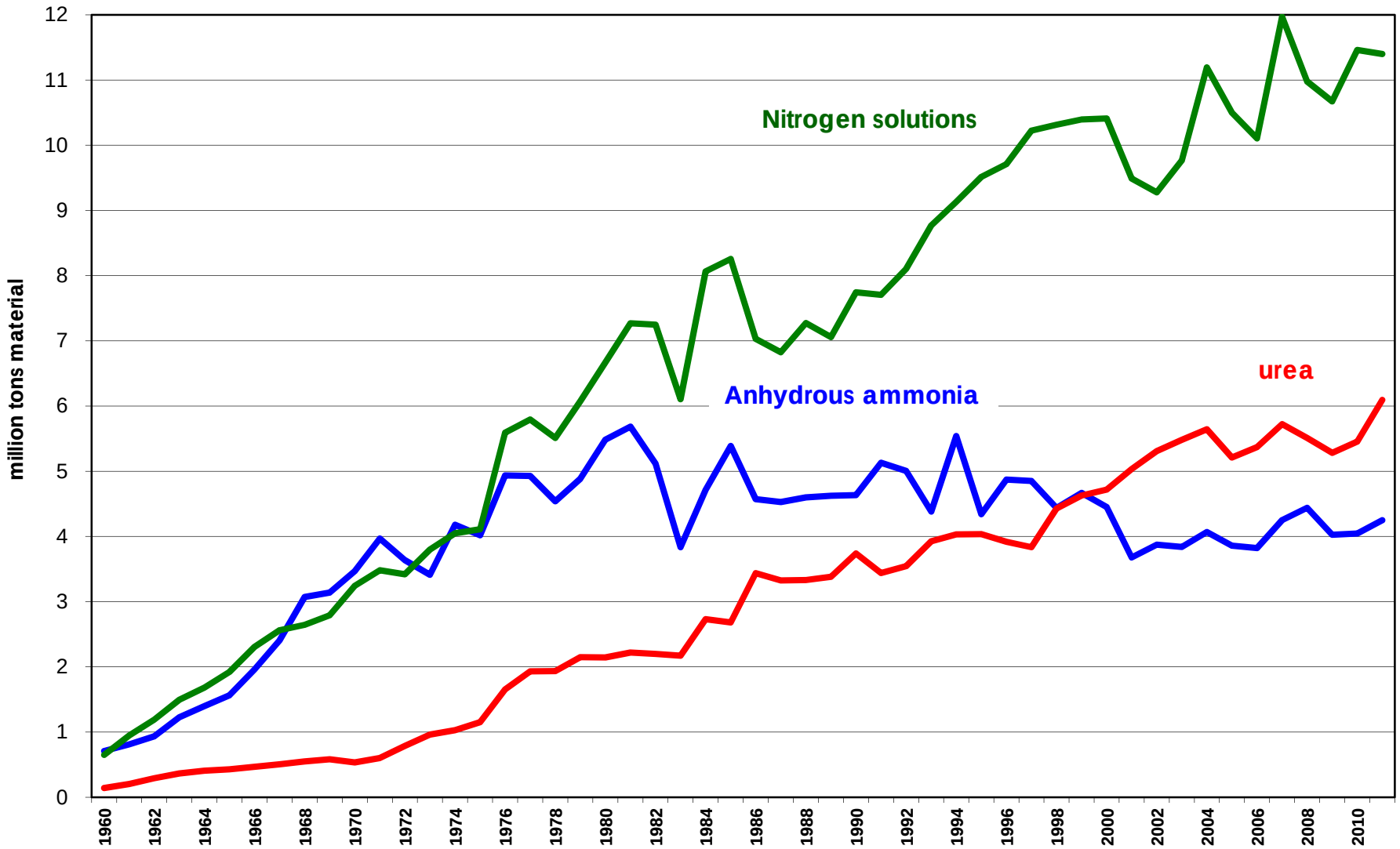

The Fertilizer Institute

Source: Commercial Fertilizers, 2011, Association of American Plant Food Control Officials and TFI, April 2013.


← Applying Anhydrous Ammonia

Side dressing nitrogen solutions →

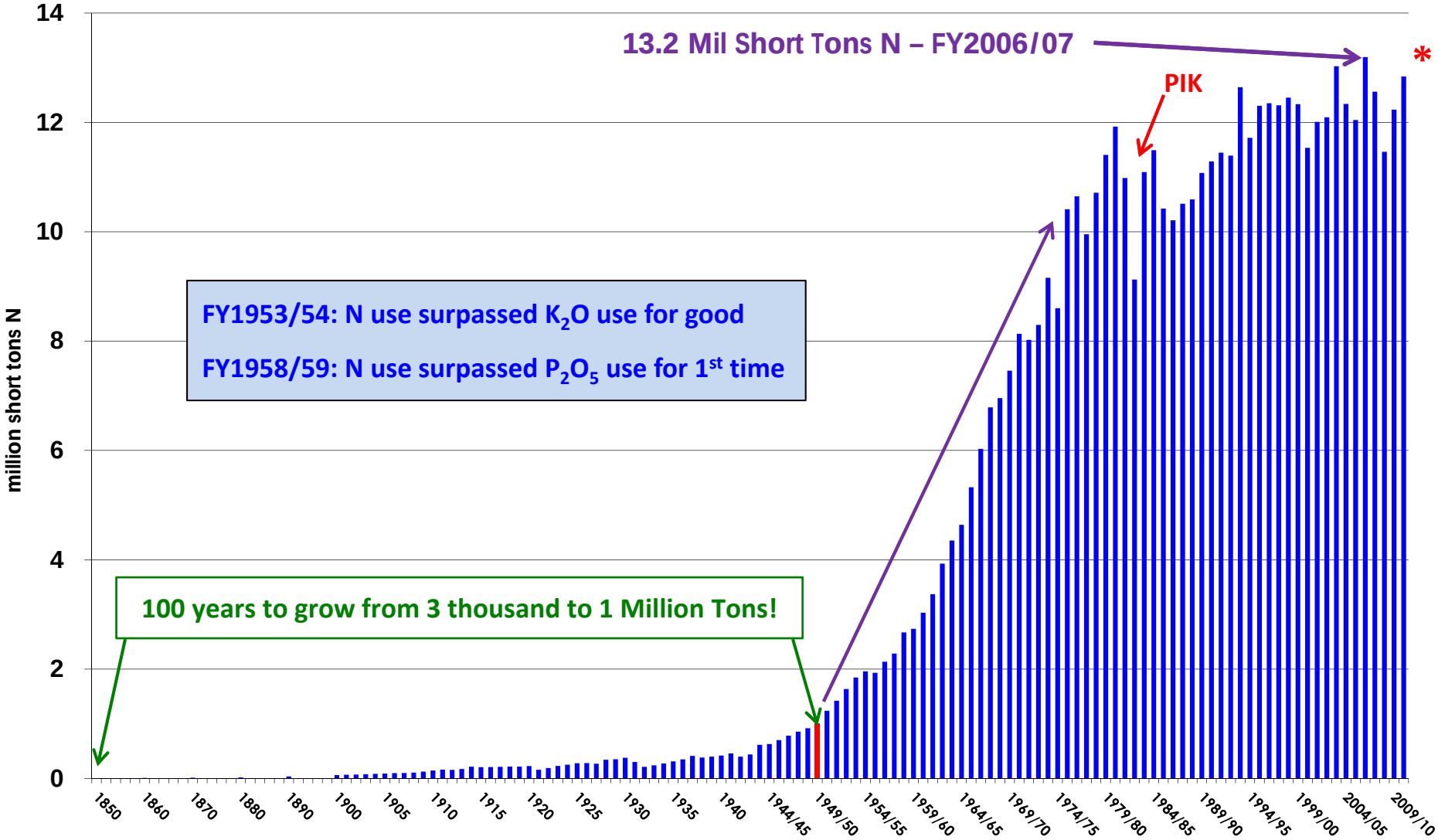
# U.S. Consumption of Selected Nitrogen Materials




The Fertilizer Institute

Source: Commercial Fertilizers, 2011 and earlier issues.

# U.S. Nitrogen Consumption:1850 – 2010/11

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Source: Historical Statistics of the United States, U.S. Census Bureau; Commercial Fertilizers, various issues.

# Media Focus

The Washington Post

**Alarming 'dead zone' grows in the Chesapeake**

By Darryl Fears, Published: July 24

A giant underwater "dead zone" in the Chesapeake Bay is growing at an alarming rate because of unusually high nutrient pollution levels this year, according to Virginia and Maryland officials. They said the expanding area of oxygen-starved water is on track to become the bay's largest ever.

This year's Chesapeake Bay dead zone covers a third of the bay, stretching from the Baltimore Ha to the bay's mid-channel region in the Potomac River, about 83 miles, when it was last measured i June. It has since expanded beyond the Potomac into Virginia, officials said.

Especially heavy flc into the bay by May Resources researche said Bruce Michael,

Forbes

Scientists: Dead Zone Stresses Gulf, Action Needed

NEW ORLEANS –

Scientists say the massive area of low oxygen in the Gulf of Mexico, known as the "dead zone" because it kills marine species, will create more problems unless fewer fertilizers are dumped into the Mississippi River.

The New York Times June 2, 2011

**Chemicals in Farm Runoff Rattle States on the Mississippi**

By LESLIE KAUFMAN

As the surging waters of the Mississippi pass downstream, they leave behind flooded towns and inundated lives and carry forward a brew of farm chemicals and waste that this year – given record flooding – is expected to result in the largest dead zone ever in the Gulf of Mexico.

Dead zones have been occurring in the gulf since the 1970s, and studies show that the main culprits are nitrogen and phosphorus from crop fertilizers

Bradenton.com

**Bill limiting local fertilizer regulation narrowly advances**

By TONI WHITT - twhitt@bradenton.com

A controversial bill that would ban cities and counties from regulating fertilizer u and sales faced surprising resistance Wednesday from House Republicans.

House Bill 457, designed to preempt local ordinances, passed the committee 8

A simil- Senate bill easily passed through committee unanimously.

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# Here's My Plan to Improve Our World — And How You Can Help

Bill Gates, Wired.com, Nov. 12, 2013

"These days I get to spend a lot of time trying to advance innovation that improves people's lives in the same way that fertilizer did."

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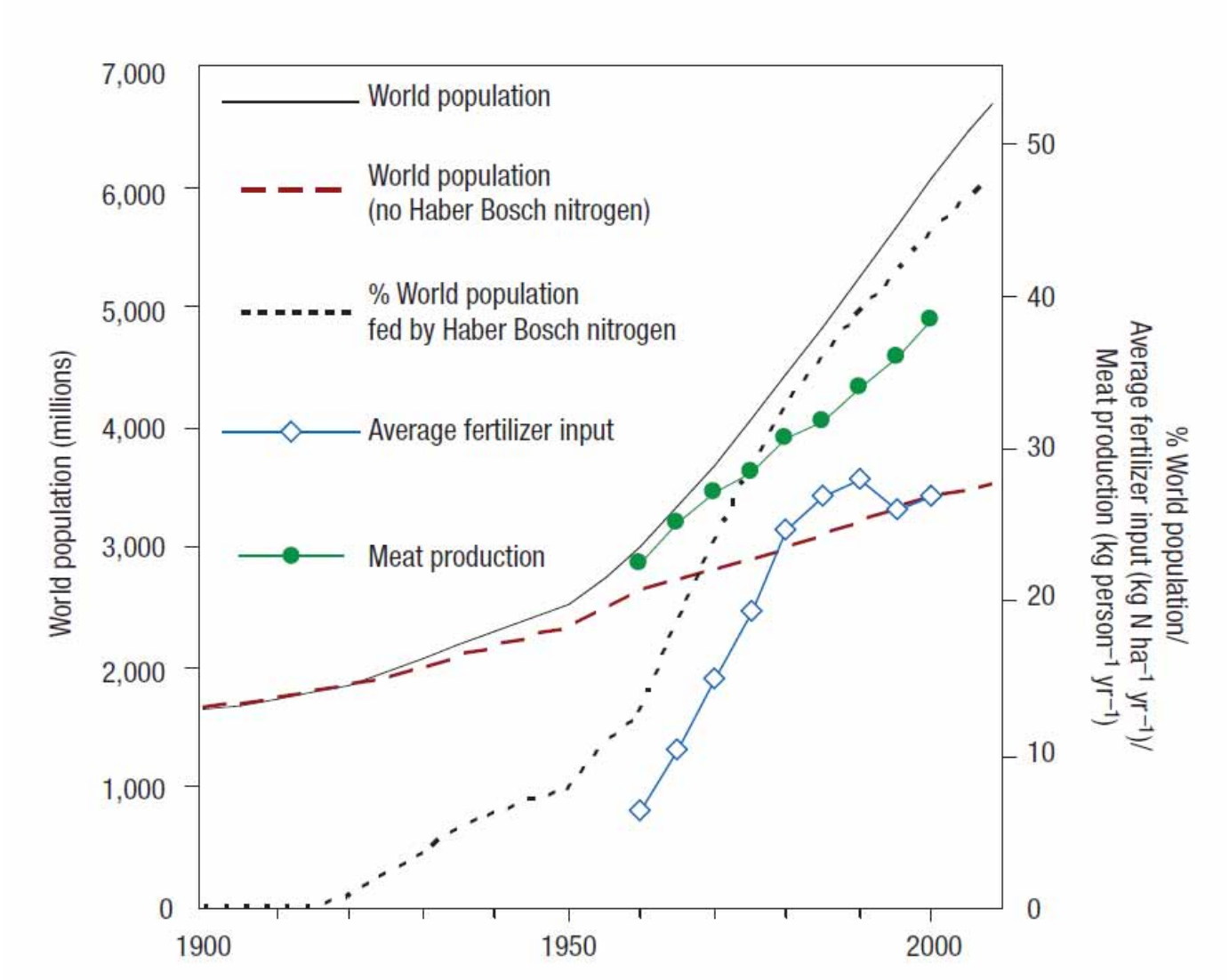
"… the lives of around half of humanity are made possible by Haber-Bosch nitrogen"

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Source: Nature Geoscience, Feature Article, Vol. 1, October 2008.

**“The Haber-Bosch process has been of greater fundamental importance to the modern world than the airplane, nuclear energy, spaceflight or television".**

**Vaclav Smil,** ***Enriching the Earth*****, 2001.**

# Thank You!

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