The Historical Development of the Haber-Bosch Process

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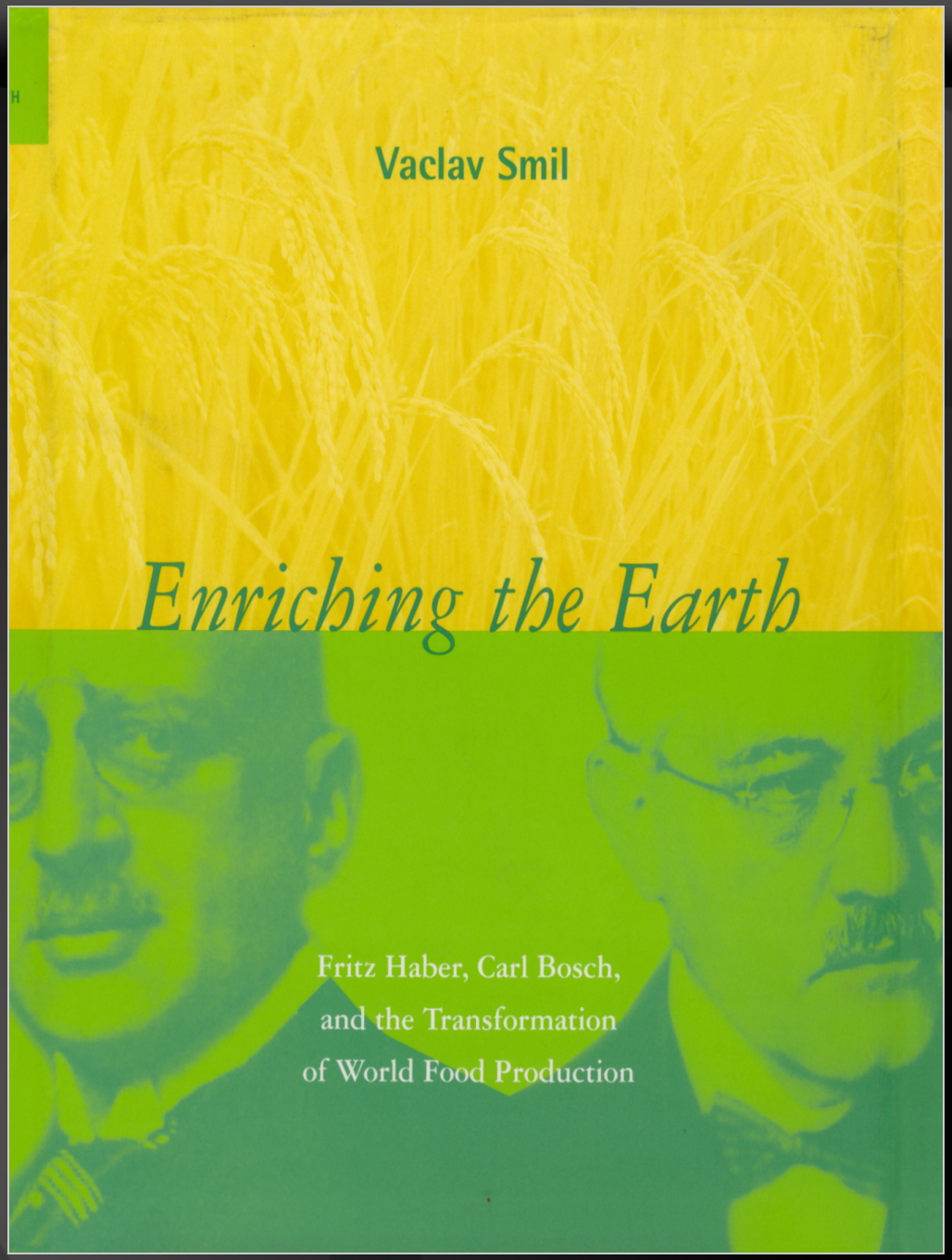
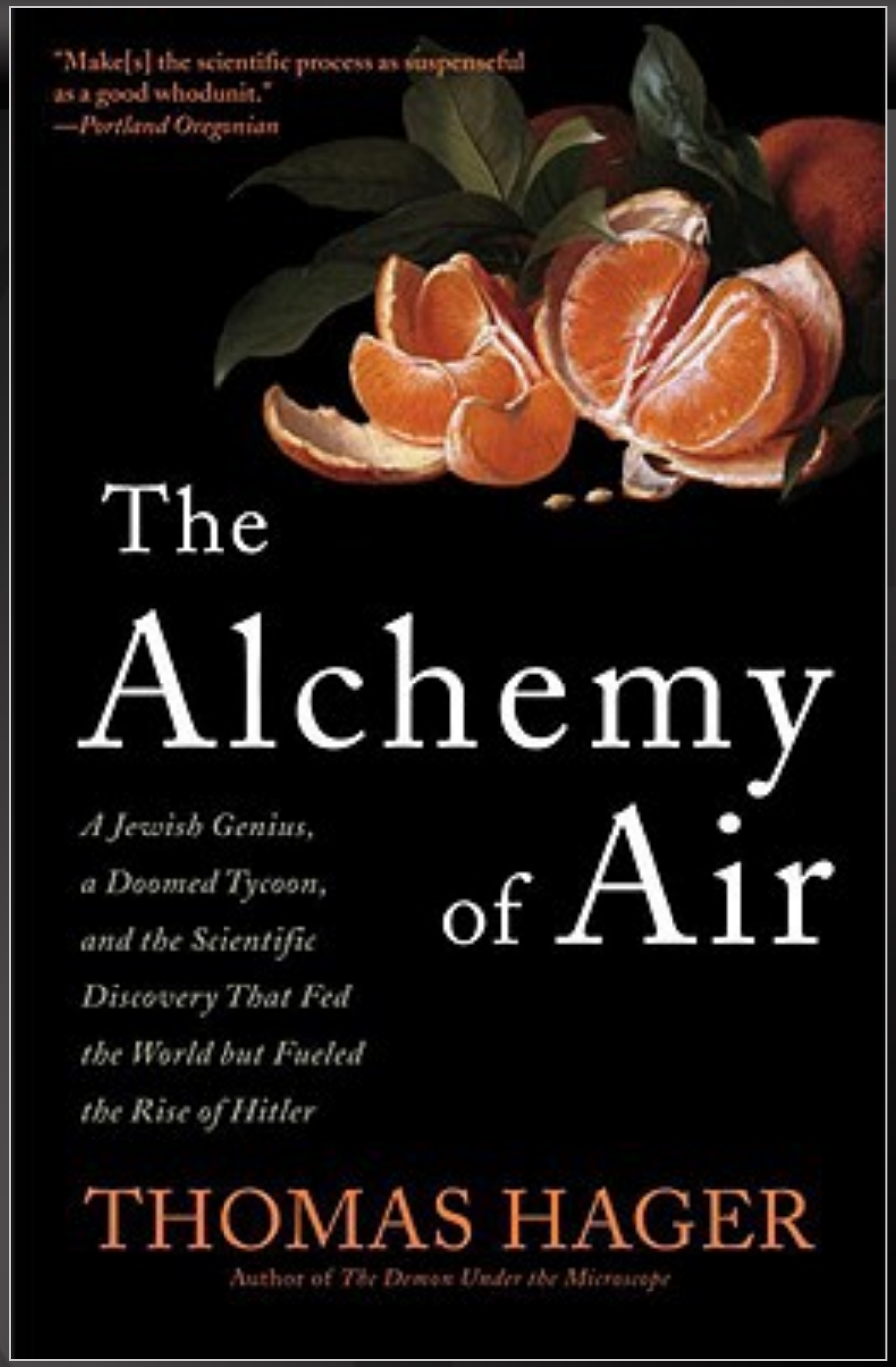
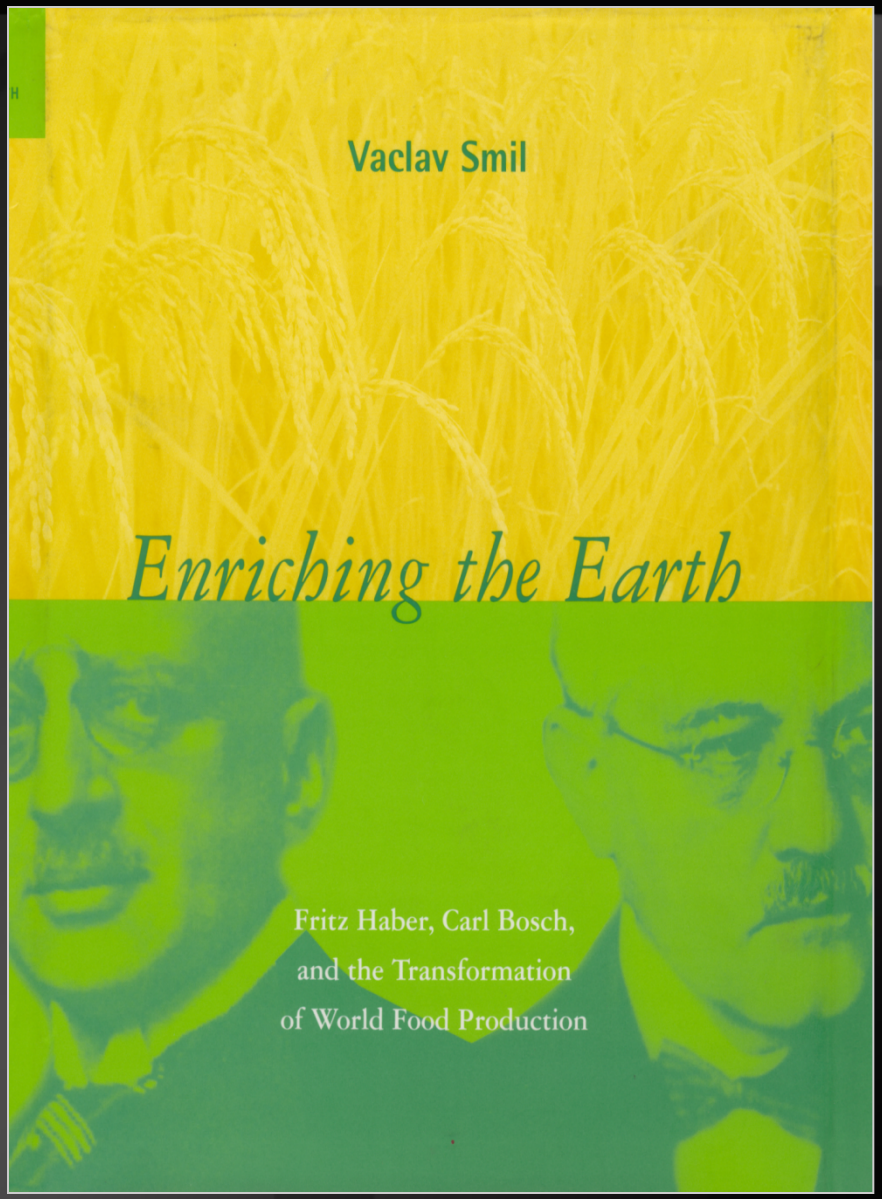

Vaclav Smil
Enriching the Earth
Fritz Haber, Carl Bosch,
and the Transformation
of World Food Production


"Make[s] the scientific process as suspenseful as a good whodunit."
—Portland Oregonian
The Alchemy of Air
A Jewish Genius, a Doomed Tycoon, and the Scientific Discovery That Fed the World but Fueled the Rise of Hitler
THOMAS HAGER
Author of The Demon Under the Microscope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The Keys to this Story

- Nitrogen is needed in all life forms as amino acids, proteins, and the many components of life machinery such as enzymes, DNA, RNA, etc. Plants require it for chlorophyll.
- Most nitrogen exists as highly non-reactive N_2 gas

Some Early History of Nitrogen

Nitrogen in the atmosphere

- Daniel Rutherford discovered N in 1772
  N would not sustain life.
- Lavoisier – considered N an elementary substance, and named it "Azote" (without life)
- Later named N "Nitrogene"

Agronomic Chemistry Knowledge of N (1836-1853)

- **Key scientists**
  - Boussingault (1802-1887)
  - Liebig (1803-1873)
  - Lawes (1814-1900) and Gilbert (1817-1901)

Jean-Baptiste Boussingault (1802-1887)

- Professor of Chemistry
- In 1836, did experiments on manuring, crop rotation, and sources of N and concluded:
  - The nutritional value of fertilizer was proportional to its nitrogen content.
  - Found N as a major component of plants.

Justus von Liebig (1803-1873)

- "Law of the Minimum", plant growth is limited by the growth factor present in the least adequate amount.
- He was at the center of discussions about Agricultural Chemistry. He "shaped the debate".
- He was wrong on two key points:
  - Soil and atmospheric ammonia supplied enough N for crops
  - Analyzing plant ash indicated the N present in crops

John Bennet Lawes (1814-1900)
Joseph Henry Gilbert (1817-1901)

- Starting 1843, they tested Liebig's mineral theory by establishing fertilized and unfertilized plots at Rothamsted.
- By 1853, there was no doubt that Liebig was wrong based on yields of wheat.
  - Plots with added **P**, **K**, **Mg**, yielded the same as unfertilized plots
  - Plots with **P**, **K**, **Mg** + **N** had double the yields.

Major N cycle contributions 1850-1900

- In 1888, two German scientists, Hellriegel and Wilfarth, reported that microorganisms associated with legumes provided the ability to fix N from the air.
- 1889, Winogradsky reported nitrification was carried out by nitrosomonas and nitrobacter.
- In 1885, Gayon and his assistants isolated two bacteria that reduced nitrate.

By 1900, the general **qualitative** aspects of the nitrogen cycle had been discovered. **Quantifying** the nitrogen cycle is an equal or greater challenge that continues today, more than 100 years later.

History of Wheat Yields in Europe

Some historical wheat yields

England, wheat yields:

- In the year 1500, 500 kg grain per hectare (contains about 10 kg N per hectare).
- Some estimates of non-symbiotic N fixation exceed 20 kg N per hectare/year.
- By the year 1850, 1000 kg grain per hectare due to widespread adoption of crop rotations, including legumes (clover, alfalfa, vetch), and intensive use of animal manures.

Source: Vaclav Smil. 2001. Enriching the Earth, MIT Press

Example: County of Norfolk, England

- An approximately constant 13% of the county was sown to legumes from 1250 to 1740.
- By 1836, this rate had become 27%, with a great shift to the use of clovers.
- Norfolk cycle of rotation
  - wheat-turnips-barley-clover

Source: Vaclav Smil. 2001. Enriching the Earth, MIT Press

The Agricultural Revolution in Northern Europe, 1750-1880

Chorley, G.H.P. 1981. Economic History 34: 71-93.

Chorley (University College of London) concluded that

"…there was one big change of overriding importance: … leguminous crops and the consequent increase in the nitrogen supply. It is not fanciful to suggest that this neglected innovation was of comparable significance to steam power in the economic development of Europe in the period of industrialization"

Other N sources for the mid 19th century

- Guano- 200,000 tons per year to England in early 1850s. US imports totaled 760,000 tons during the 1850s
  - The best contained 15% N, the worst 5-6 % N
  - Quality dwindled with time from less desirable sources
- Sodium nitrate from Chile
  - 300,000 tons exported by late 1870s
  - Up to 1.3 Mt in 1900 and a max of 2.5 Mt 1913
  - In the US, about half used for explosives
  - 1903 forcast- reserves to be gone by 1938

Source: Vaclav Smil. 2001. Enriching the Earth, MIT Press

William Crookes' speech

- As president of the British Assn for the Advancement of Science, he spoke about the "wheat problem" (*Nature Sept 8, 1898*)
  - "all civilized nations stand in deadly peril of not having enough to eat"
  - "our wheat-producing soil is totally unequal to the strain put upon it"
  - One of the best speeches at the turn of the century caused a furor among politicians and economists and agricultural experts.

1900: Wilhelm Ostwald, German scientist, claimed to have produced ammonia using an iron catalyst at high temperature and pressure.

Wilhelm Ostwald (1853-1932)

$$N_2 + 3H_2 = 2\ NH_3$$

Image Source: http://www.google.com/imgres?imgurl=http://upload.wikimedia.org/wikipedia/commons/d/d7/Wilhelm_Ostwald.jpg&imgrefurl=http://en.wikipedia.org/wiki/File:Wilhelm_Ostwald.jpg&h=825&w=750&sz=134&tbnid=OjKsj3DghfxioM:&tbnh=90&tbnw=82&prev=/search%3Fq%3Dwilhelm%2Bostwald%26tbm%3Disch%26tbo%3Du&zoom=1&q=wilhelm+ostwald&docid=t9I9ZGbpI8jOlM&sa=X&ei=RfeKTuq6K8i9tgfqr5isAw&ved=0CEsQ9QEwBg&dur=6

Carl Bosch – was tasked by BASF, a German chemical company, to check Ostwald's claim.

Bosch concluded that Ostwald's experiment produced ammonia impurities.

Carl Bosch (1874-1940)

Image Source: http://www.britannica.com/EBchecked/topic/74581/Carl-Bosch

Fritz Haber

- Received doctorate in 1891
- Published 50 papers from 1900-1905
- Became professor of physical and electro chemistry in 1906.

Fritz Haber
(1868-1934)

Image Source:
http://www.nobelprize.org/nobel_prizes/chemistry/laureates/1918/haber-bio.html

Fritz Haber – *in 1904*

- First experiments on reaction of nitrogen with hydrogen to form ammonia.
- Studied conditions of temperature and catalysts at atmospheric pressure
- Low ammonia yields. Haber concluded that the gas reaction to produce ammonia was not commercially possible.
- Paper published in 1905.

Walther Nernst

Nernst, Ostwald's former student, did ammonia reaction and obtained different yields than those reported by Haber.

1907: Nernst publicly humiliated Haber with very negative remarks during a scientific society meeting.

Walther Nernst (1864-1941)

Image source: http://en.wikipedia.org/wiki/Walther_Nernst

1907: Haber restarted his experiments and included effect of pressure, temperature and catalyst.

1908: BASF agrees to generously provide funding for research on the ARC process. BASF also reluctantly agrees to fund research on NH_3 synthesis.


GERMANY
DENMARK
BALTIC SEA
North Frisian Islands
NORTH SEA
Lübeck
Hamburg
Schwerin
Elbe Ry
Bremen
POLAND
Hanover
Berlin
NETHERLANDS
Münster
Harz Mountains
Magdeburg
Leuna
Düsseldorf
Kassel
Leipzig
BELGIUM
Rhine
Cologne
Bonn
Weimar
Dresden
Rhine Valley
Frankfurt
LUXEMBOURG
CZECH REPUBLIC
Ludwigshafen
Nuremberg
Heidelberg
Karlsruhe
Danube Ry
FRANCE
Stuttgart
Tübingen
BAVARIA
Freiburg
Lake Constance
Munich
AUSTRIA
0 100 km
0 60 miles
Füssen
SWITZERLAND

1909: Haber continues his work with gradual improvements. He reports success to BASF in March 1909.

Conditions:

100 atm pressure

500°C

Osmium catalyst

Time Line

- March 23, 1909- Haber reported by letter to BASF his success in NH_3 synthesis. He also recommended buying all the osmium BASF could find.
- March 26, 1909- Haber meets with BASF reps Heinrich von Brunck, August Bernthsen and Carl Bosch to discuss if the process could be brought to an industrial scale.
- July 2, 1909- Haber demonstrated success of the process at Karlsruhe to BASF personnel Alwin Mittasch and Julius Kranz.

Industrializing ammonia synthesis

Countries that built Haber Bosch Plants in early 1920s:

1. France
2. England
3. U.S.

http://www.britannica.com/EBchecked/topic/74581/Carl-Bosch

The Oppau plant after the explosion of 1921.
© BASF Corporate Archives, Ludwigshafen/ Rhein

Source:
http://www.makingthemodernworld.org.uk/stories/the_second_industrial_revolution/05.ST.01/?scene=5

Nobel Prize Winners

Carl Bosch

Frederick Bergius

The Nobel Prize in Chemistry 1932 was awarded to Carl Bosch and Frederick Bergius *"for their services in originating and developing chemical high-pressure methods"*.

Image sources:
http://www.britannica.com/EBchecked/topic/74581/Carl-Bosch
http://upload.wikimedia.org/wikipedia/commons/b/bc/Bergius.jpg

Science and Politics

Nobel Prize Winner

The Nobel Prize in Chemistry 1918 was awarded to **Fritz Haber** *"for the synthesis of ammonia from its elements"*.

The Efficiency of a Modern Ammonia Production Plant

- About 0.6 to 0.7 tons natural gas yields one ton of NH_3
- The overall reaction
  - $7CH_4 + 10\ H_2O + 8N_2 + 2\ O_2 = 16\ NH_3 + 7\ CO_2$
- Overall, slightly exothermic process
  - About -110,000 kcal per ton of NH_3 gas.
  - Heating value of this much CH_4 would be around -5,000,000 kcal/ton of ammonia

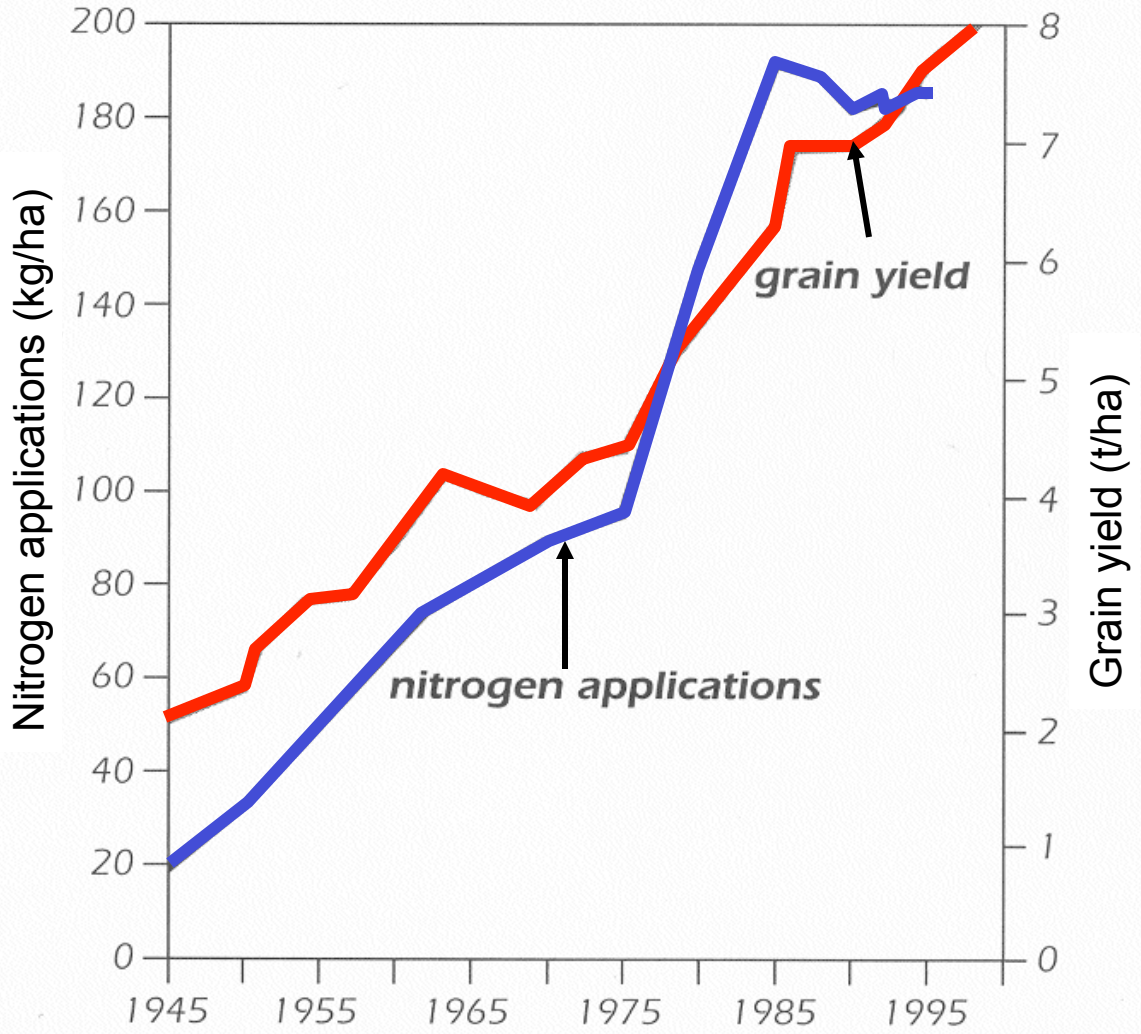
Fertilizer Manual, 1979. IFDC

Coastal Bermudagrass Tifton, GA; 24 week growth

N rate Kg/ha	Delta DM Kg/ha	CH_4 equiv to fix N Kg/ha	DM/CH_4
112	7,261	73	99
336	15,043	218	69

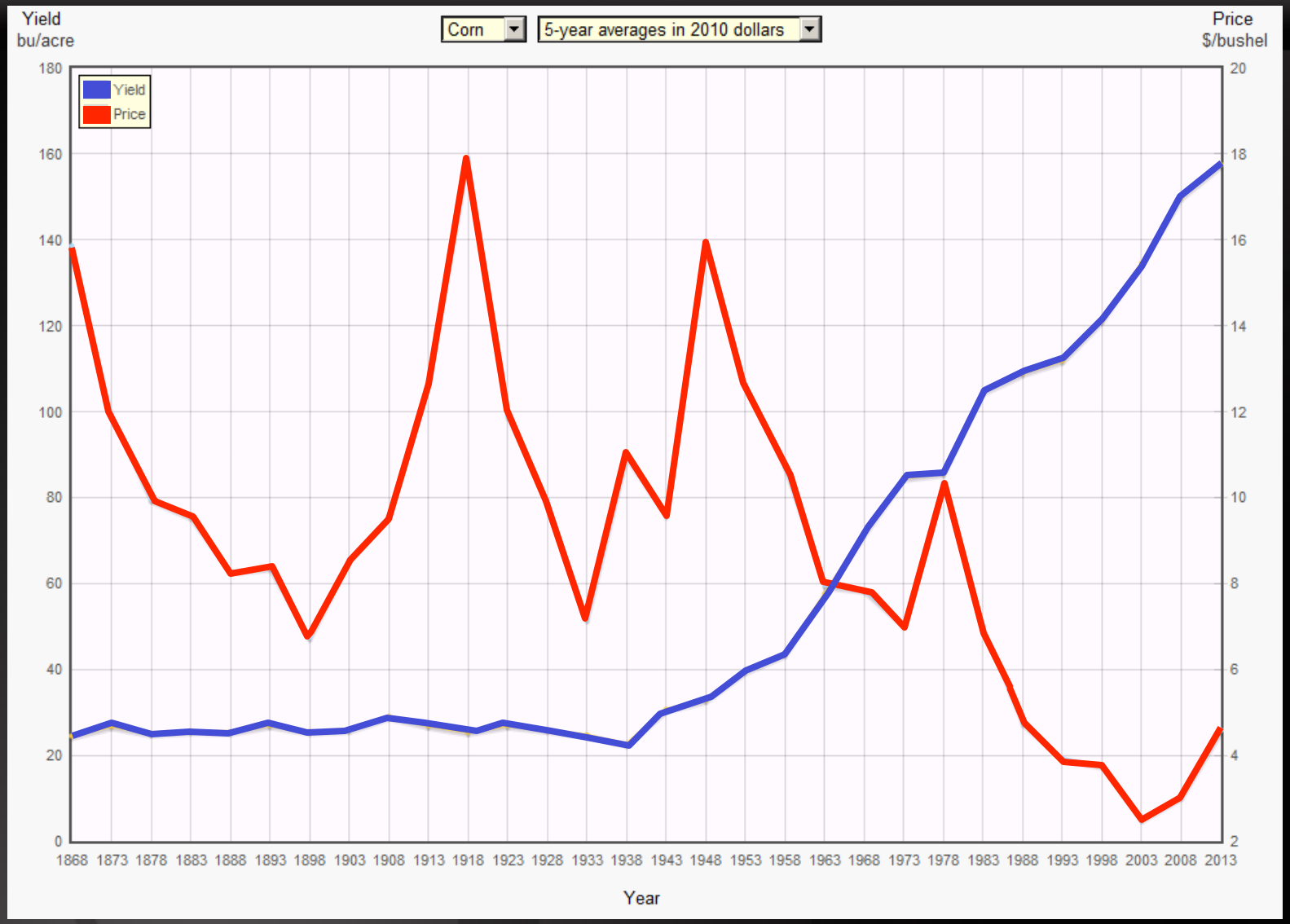
Prine and Burton, 1956. Agron. J. 48:296-301

Modern crop yields



Nitrogen applications and yields of English winter wheat, 1945-1998.

Source: Vaclav Smil. 2001. Enriching the Earth, MIT Press


Yield
bu/acre
Corn
5-year averages in 2010 dollars
Price
$/bushel
Yield
Price
180
160
140
120
100
80
60
40
20
0
20
18
16
14
12
10
8
6
4
2
1868 1873 1878 1883 1888 1893 1898 1903 1908 1913 1918 1923 1928 1933 1938 1943 1948 1953 1958 1963 1968 1973 1978 1983 1988 1993 1998 2003 2008 2013
Year

USDA ERS

Nitrogen Consumption in Agriculture

U.S.

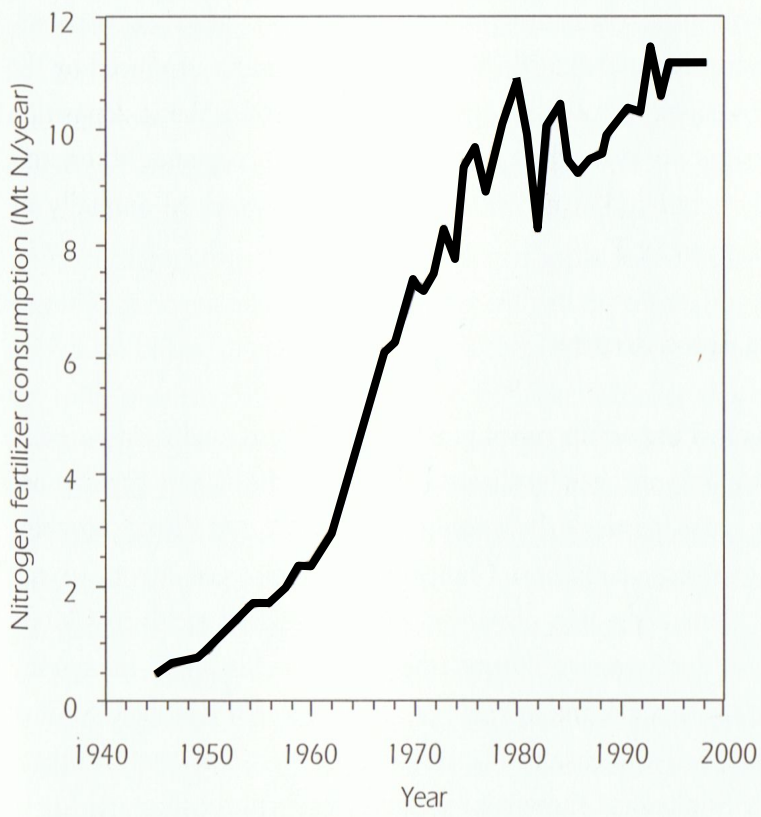


Figure 7.9
Consumption of nitrogen fertilizers in the U.S. agriculture, 1945–1997.

World

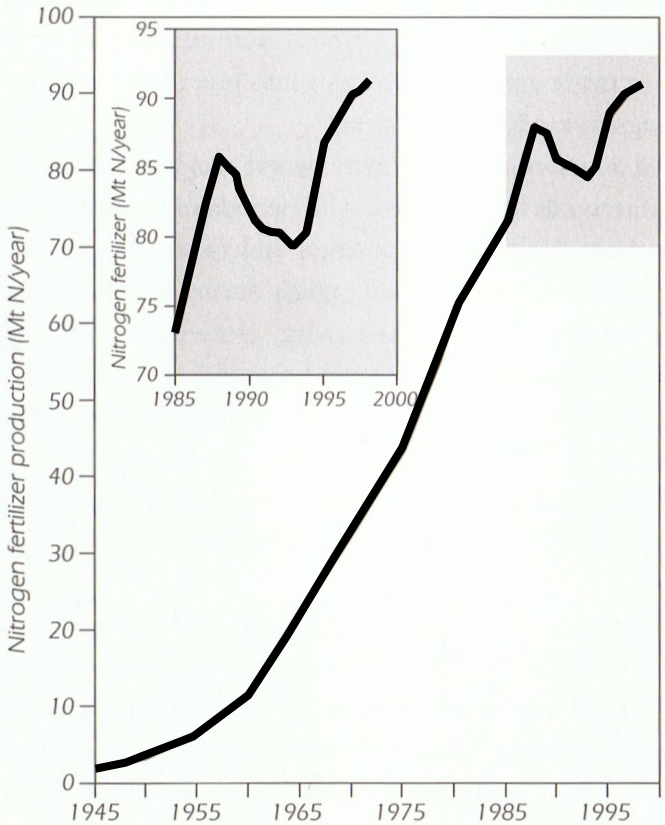
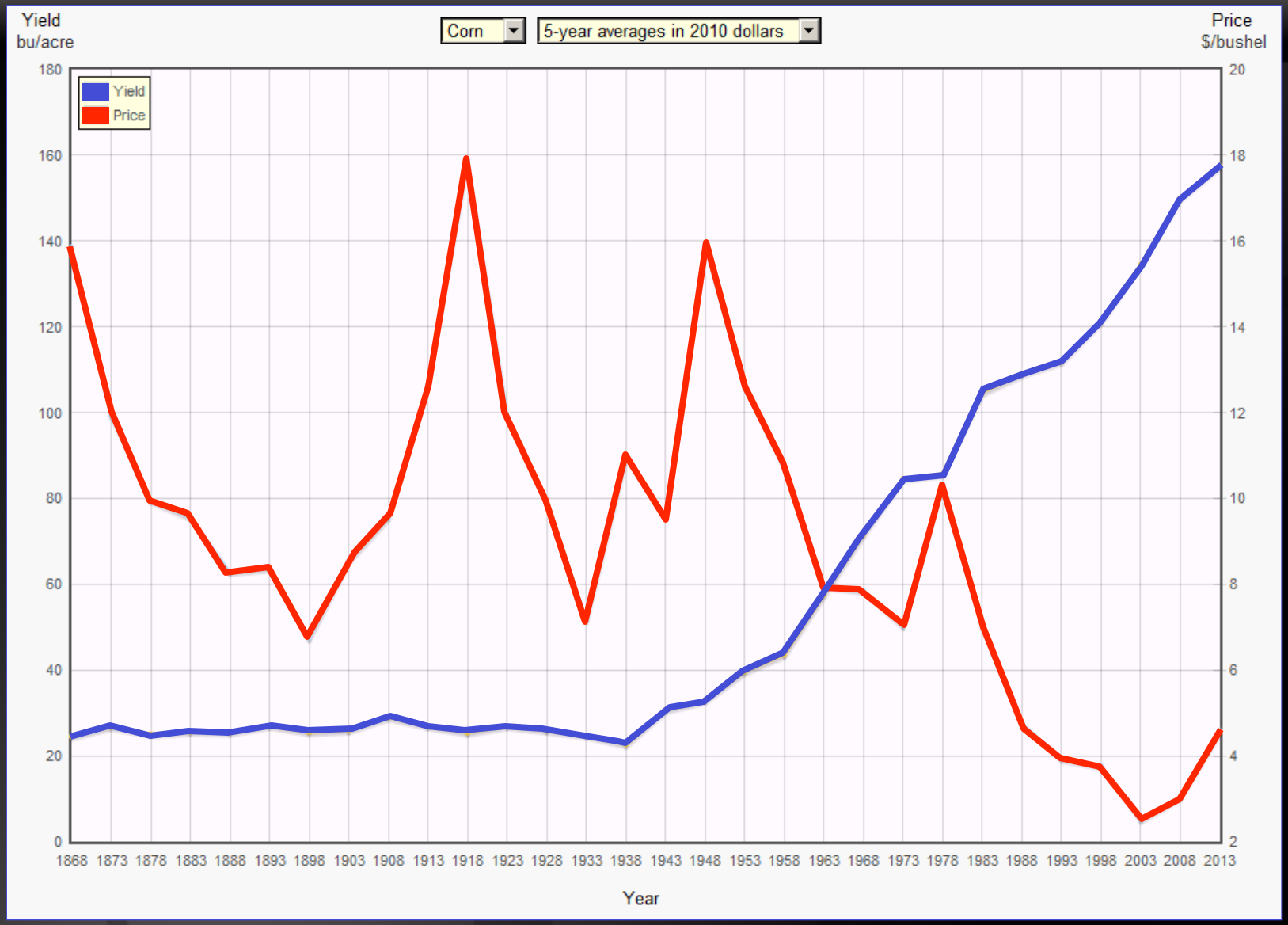
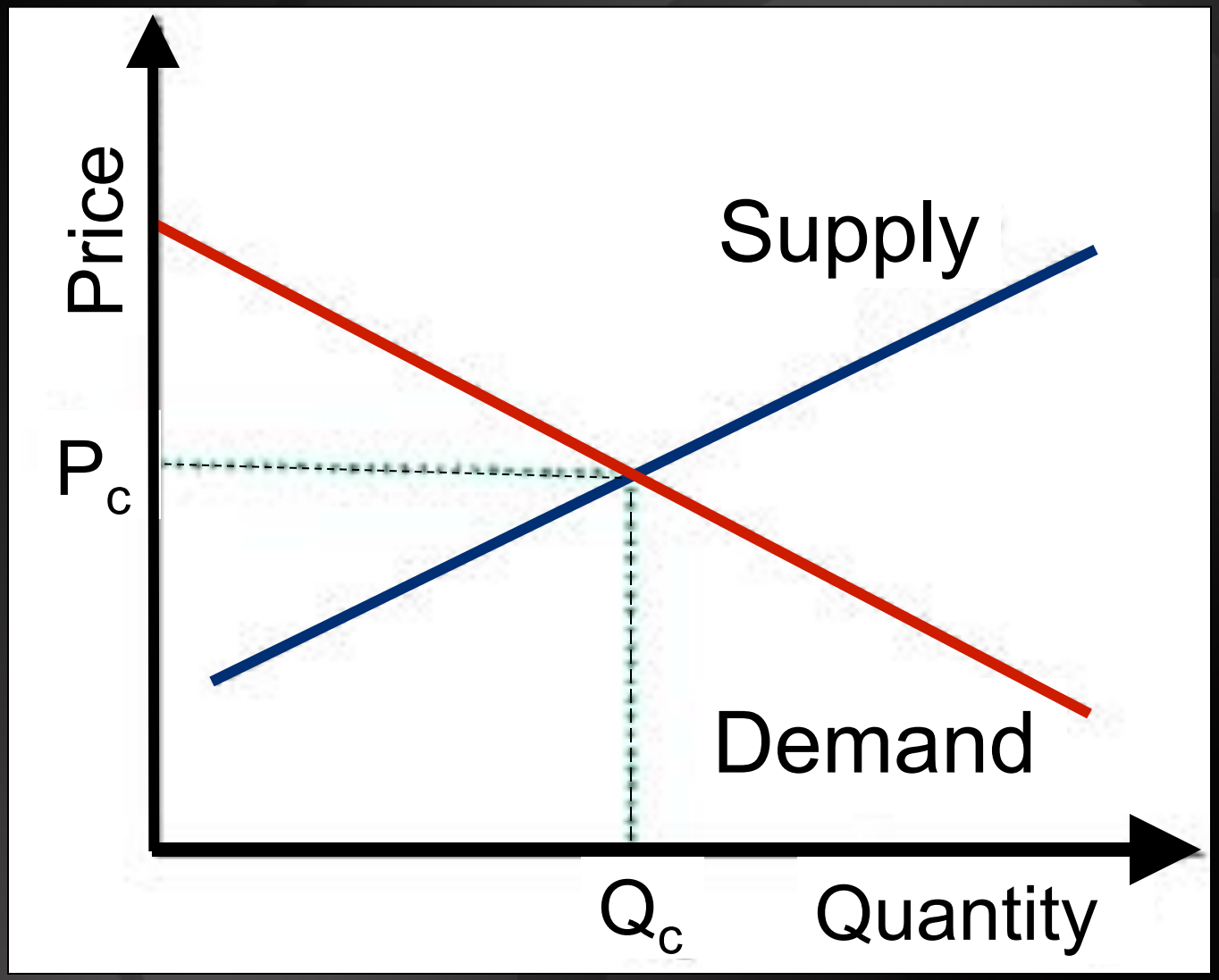


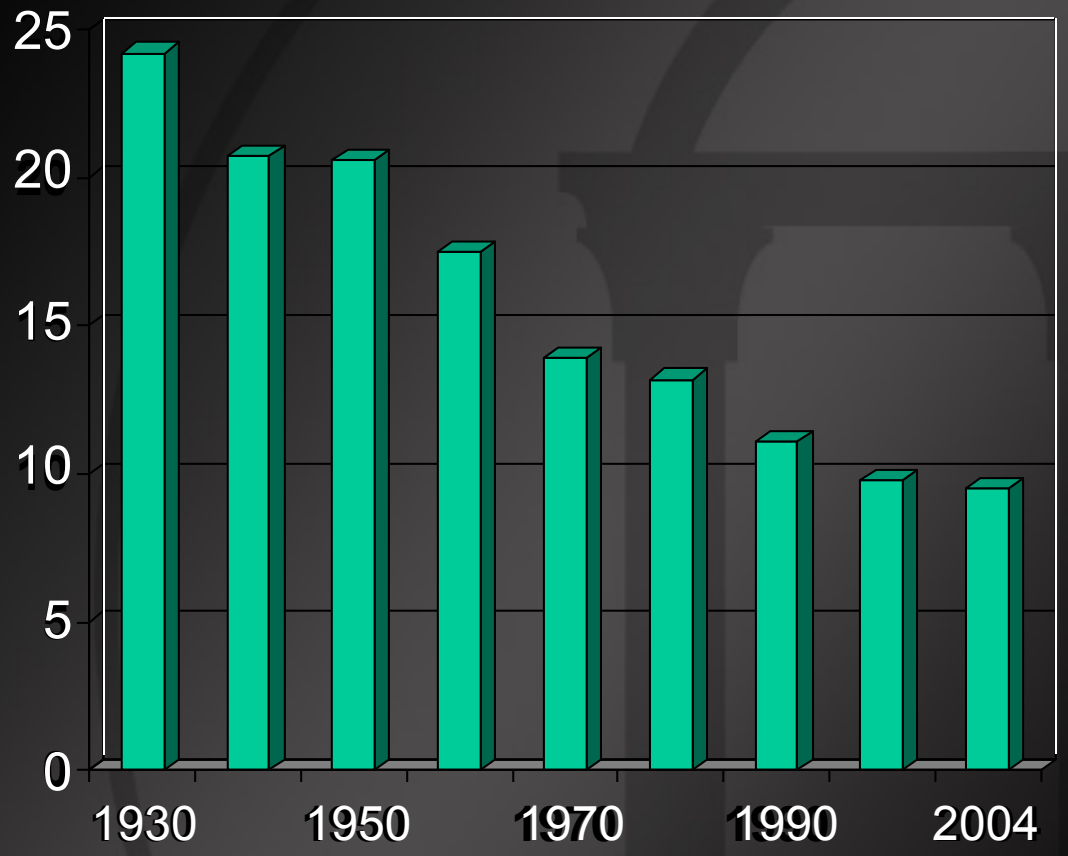
Figure 6.2
Global production of ammonia-based nitrogen fertilizers, 1945–1998.

Source: Vaclav Smil. 2001. Enriching the Earth. MIT Press


Yield
bu/acre
Corn
5-year averages in 2010 dollars
Price
$/bushel
Yield
Price
180
160
140
120
100
80
60
40
20
0
20
18
16
14
12
10
8
6
4
2
1868 1873 1878 1883 1888 1893 1898 1903 1908 1913 1918 1923 1928 1933 1938 1943 1948 1953 1958 1963 1968 1973 1978 1983 1988 1993 1998 2003 2008 2013
Year

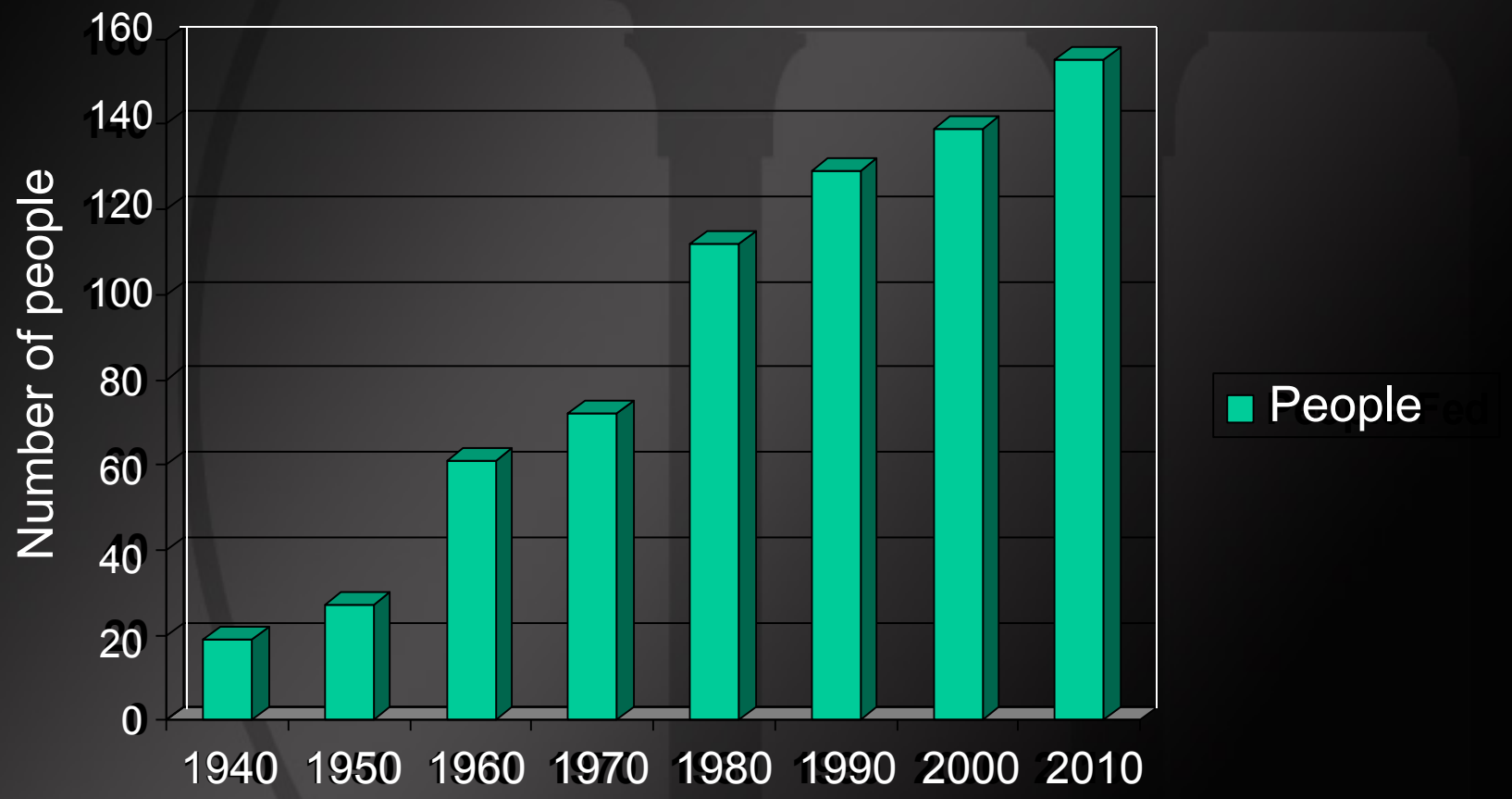
USDA ERS


Price
Supply
P_c
Demand
Q_c
Quantity



USDA, Economic Research Service

People Fed by One Farmer, US



American Farm Bureau Federation

CHINA- The Tragedy of Mao's Great Leap Forward, 1958-1962

- Move people to cities to industrialize.
- Produce Food in Large Communes
- Droughts and Floods
  - 30 million people starved

CHINA, after President Nixon's visit in 1972

- Trade was opened with the Western Countries.
  - The first business- China purchased 13 of the world's biggest and most efficient Haber-Bosch ammonia plants.

Thomas Hager. 2008. The Alchemy of Air, Three Rivers Press

Unintended Consequences

Fixation of N_2 due to human activity (Vitousek et al., 1997, Science 277:494-499)

- Industrial fixation of ammonia - 100 Mt
- Soybeans, alfalfa, etc. - 40 Mt
- Burning of fossil fuels - 20 Mt
- Total - 160 Mt
  - This is approximately 55-60% of all fixed nitrogen. In other words, humans have more than doubled the amount of fixed N in the past 100 years.

Losses from ag production systems that influence other ecosystem processes

- Losses of nitrate by leaching (eutrophication of marine environ. Hypoxia)
- Losses of ammonia from fertilizers and from animal wastes (eutrophication and soil acidification).
- Losses of N_2O by denitrification and nitrification (greenhouse gas and global warming)

In order to optimize crop use of N

- Apply the correct amount of N fertilizer for each field (or areas of fields).
- Apply N as close to crop use as possible.
- Use the best N source and method of application for the conditions.
- Manage irrigation to optimize N.

Apply the correct amount of N to the crop.