

**"INDUSTRIAL METABOLISM OF NITROGEN"**

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# INDUSTRIAL METABOLISM OF NITROGEN

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## Abstract

This paper quantitatively reviews the sources, production processes and economic uses of nitrogen-based chemicals, especially ammonia and its derivatives. It attempts to account for production losses, by species, and for losses in use, especially in agriculture, using the materials balance approach. It also discusses the sources of  $\text{NO}_x$  via high temperature combustion processes, especially internal combustion engines and thermal power plants. Data is presented mainly for the U.S. in 1988. Our results are compared with other estimates.

## Introduction

Inorganic Nitrogen ( $\text{N}_2$ ) is a colorless, odorless, tasteless gas which constitutes almost 80% of the atmosphere. In this form it is chemically rather inert and inaccessible to living organisms, as well as other key chemicals in living cells. However, nitrogen is essential to organic life. Amino acids are nitrogenous compounds that are the basic building blocks of all proteins. Similarly, the basic building blocks of DNA (thymine, cytosine, adenine and guanine) all consist of single or double rings of carbon and nitrogen atoms, with various side chains. Nitric oxide (NO) is a neuro-transmitter. However, the most reduced form of nitrogen, ammonia ( $\text{NH}_3$ ), is an alkali. It is also quite toxic to animals at high concentrations. However, all known bio-fixation pathways convert di-nitrogen first to ammonia. Similarly, all pathways to the synthesis of amino acids begin from ammonia and evolve glutamic acid and aspartic acid as the primary building blocks for amino acids and proteins.

On the other hand, the most oxidized stable form of nitrogen is the compound  $\text{N}_2\text{O}_5$ , which reacts with the water molecule to form nitric acid  $\text{HNO}_3$ . The natural tendency toward thermodynamic equilibrium, in an oxidizing environment, would be for reduced nitrogen in the -3 valence state ( $\text{NH}_3$ ) to be oxidized gradually to the +5 valence state (nitrate ion,  $\text{NO}_3^-$ ). The result would be an acid ocean, leaving an atmosphere with no free oxygen left in it. No life on such an earth would be possible. Hence life itself depends on the continuing stability of a natural cycle — the nitrogen cycle — which biologically reduces oxidized forms of nitrogen. This cycle evolved over billions of years to a (nearly) balanced and quasi-stable state. However, as will be seen, the cycle is now being rapidly unbalanced as a result of human activity.

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Hereafter we use the conventions: metric ton = MT; thousand metric tons = KMT; million metric tons = MMT.

## Sources and Production of Fixed Nitrogen for Industry

Human interference in the natural nitrogen cycle began with the cultivation of legumes and the deliberate recycling of animal manures to soil. However, the magnitude of this intervention was small and remained so until relatively modern times. It would not be unreasonable to assume that the nitrogen cycle itself remained in balance, through most of human history, although the total amount of biologically available nitrogen<sup>1</sup> in circulation has probably increased gradually. In the last century, however, this increase has accelerated. For a century, beginning about 1840, sodium nitrate (saltpeter) was mined in Chile. Nitrogen fertilizer accounted for a minor part of the use of this material (13% in the U.S. in 1910); most of it was used for explosives (41%), dyestuffs (12%) and for other chemicals (25%) with 5% unaccounted for and 4% going to glass manufacturing. However, total Chilean production peaked at about 450 KMT in the 1920's.

The first commercial process for direct nitrogen fixation was the so-called Birkeland-Eyde process, developed in Norway and first commercialized in 1904. This process emulated the natural process by which nitrogen is oxidized in the atmosphere in the presence of an electric arc (i.e. lightning). A competing process, developed around 1905, was the cyanamid process, yielding calcium cyanamide ( $\text{CaCN}_2$ ) from limestone, coke and atmospheric nitrogen. The calcium cyanamide is dissolved in water to form urea and ammonia.

It is interesting to note that in 1920 there were five different anthropogenic sources of biologically available ("fixed") nitrogen, producing a world total of just over 1.55 million metric tons of N-content<sup>2</sup>. Of this, Chilean saltpeter (still the largest source) accounted for only 30%. The second largest (26.6% in 1920), was ammonium sulfate from by-product coking of coal. This was a process developed in Germany in the 1880's by Koppers, which is still in use, although nowadays the main by-product is coke-oven gas. In fact, about 0.86 kg of  $\text{NH}_3$  can be extracted from a ton of bituminous coking coal [Russell & Vaughan 1976, Table 3.2], along with 178 kg of high-BTU gas (8800 cubic feet). Thus, production of 1 mcf of gas also yielded up to 98 kg of  $\text{NH}_3$ . Later ammonia was produced in larger quantities from the coking of coal for the steel industry, but still as a byproduct. Its output could not be expanded above the limited amounts available from coal usage.

By 1920 the third largest source of synthetic fixed nitrogen (20.9%) was calcium cyanamid. This process was still commercially significant in the 1950's, but it was then obsolescent. The last cyanamide plant in the Western world closed in June, 1971.

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<sup>1</sup> Biologically available inorganic nitrogen corresponds with "odd-nitrogen", i.e. nitrogen compounds or radicals with 1 or 3 nitrogen atoms combined with hydrogen, oxygen or carbon. Principal examples include ammonia/ammonium ( $\text{NH}_3/\text{NH}_4$ ), nitrite/nitrate ( $\text{NO}_2/\text{NO}_3$ ), and cyanide (CN).

<sup>2</sup> For a detailed discussion and breakdown see A.J. Lotka [Lotka 1956, Chap. XVIII].

The fourth source of fixed nitrogen in 1920 (19.8%) was synthetic ammonia ( $\text{NH}_3$ ), made by the so-called Haber-Bosch process, developed by the German firm BASF and commercialized in 1913. Karl Bosch adapted this process to industrial production, largely to meet the demand for explosives during World War I. During World War II many ammonia plants were constructed to produce the nitrogenous materials for explosives (almost all of which are nitrogen-based) as well as fertilizers. The availability of substantial capacity for synthesizing ammonia gave rise to a growing nitrogen fertilizer industry in the U.S. after WWII.

By 1920 the Birkeland-Eyde process was already obsolete, because of its dependence on very cheap electricity, and then accounted for only 1.5% of synthetic nitrogen.<sup>3</sup>

From a world total of 1.55 MMT (N) in 1920, the use of synthetic nitrogen has skyrocketed, especially after the second world war. The world total for 1948-49 was 3.3 MMT, rising to 4.7 MMT just four years later [Shreve 1956, Chapter 20]. 1989 world production of fixed nitrogen, almost all of it in the form of synthetic ammonia, was close to 120 MMT, i.e. 99 MMT N-content. The so-called Haber-Bosch process is the basis for almost all the ammonia manufactured today. The process involves direct combination of nitrogen and hydrogen at high pressure, in the presence of a catalyst of iron oxide plus small quantities of cerium and chromium at high pressure and temperature. There have been many improvements to the basic process utilizing various catalysts and increasingly high temperatures and pressures.

Before 1950 the major source of hydrogen for the synthesis of ammonia was the reaction of coal or coke and steam via the water-gas process. A small number of plants used water electrolysis or coke-oven by-product hydrogen. After 1950 the major source of hydrogen has been natural gas obtained by steam reforming of natural gas (or, less commonly, oil, coal or lignite). The partial oxidation process is also used to produce hydrogen from natural gas and other liquid hydrocarbons. As of 1975, 75 to 80 percent of the world supplies of hydrogen for the manufacture of ammonia came from steam-reforming of hydrocarbons, of which 65% was from natural gas. The importance of natural gas has continued to grow.

The original source of synthetic nitrogen chemicals has always been air, which is already 80% pure. It is fairly easy to purify the nitrogen further by letting the oxygen react with some other substance, leaving an oxide ( $\text{H}_2\text{O}$  is the simplest) that is easy to remove by condensation or solvent extraction. Originally, the nitrogen was obtained either from a liquid-air separation plant or by burning a small amount of hydrogen in the synthesis gas. Modern ammonia plants eliminated the above process steps by the use of secondary reforming, a process in which methane is burned in air in the amount required to produce a 3:1 mole ratio of hydrogen to nitrogen synthesis gas.

The Haber-Bosch process as used in the U.S. today is based on the passage of a mixture of air and natural gas over a catalyst at very high pressure. Under the required conditions the methane in the gas is cracked and the carbon reacts with oxygen to form  $\text{CO}_2$  while the hydrogen and nitrogen combine in the presence of a catalyst to form ammonia ( $\text{NH}_3$ ). See *Figure 1*. (The subsequent processes to obtain key derivatives are shown in *Figure 2*). There

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<sup>3</sup> However, in an hypothetical future world in which hydrocarbons are scarce but electricity (from fusion reactors or the sun) is inexpensive, the Birkeland-Eyde process could conceivably be revived.

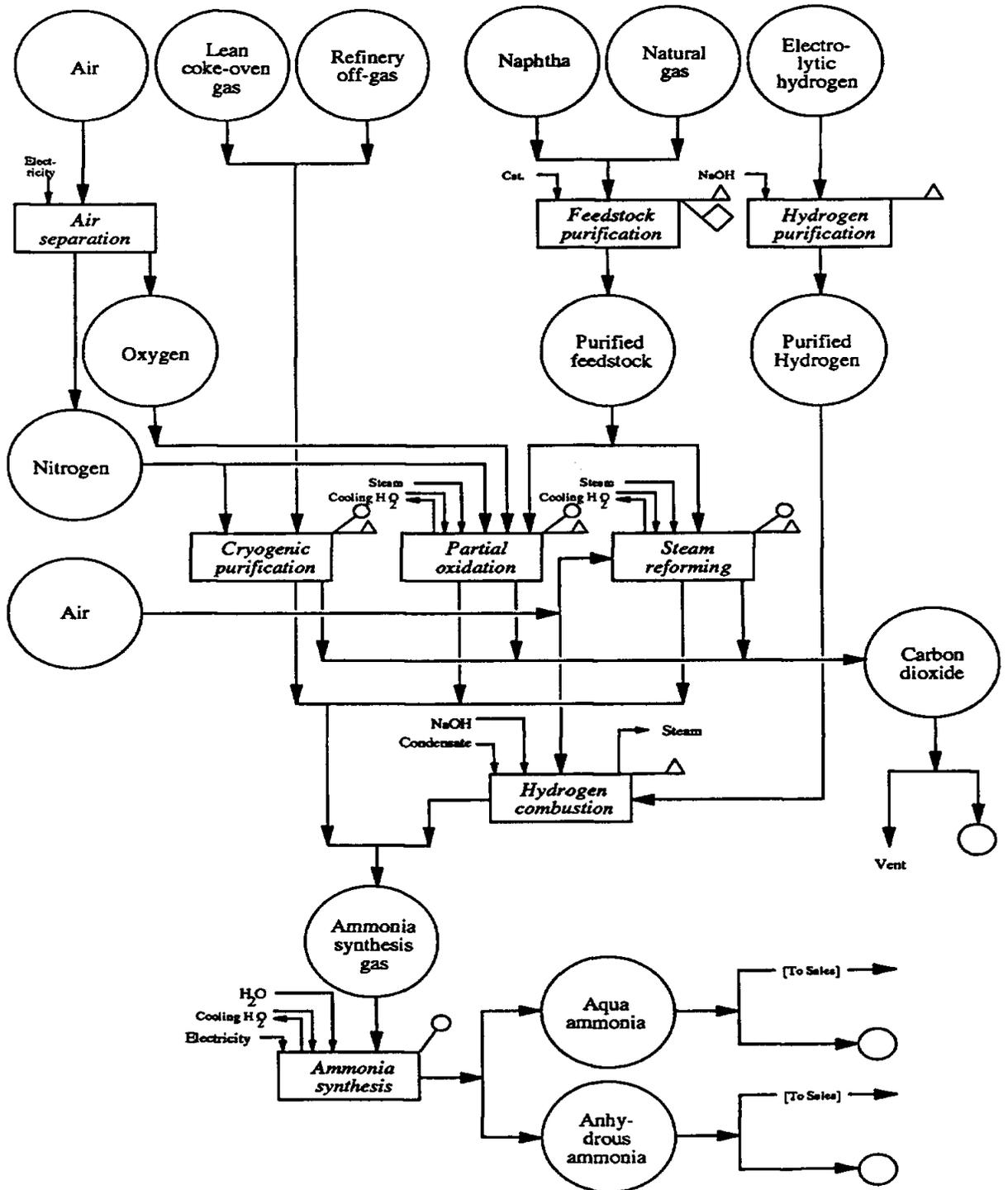


Figure 1: Materials-Process Relationships for Ammonia Synthesis  
 Source: [Muehlberg et al 1977; p. 30]

are several variations of the basic process depending on (1) the separation of air to produce nitrogen or (2) the removal of the oxygen by combustion to leave a nitrogen CO<sub>2</sub> material that can then be separated. While the wartime plants were mainly in the 200-300 tonne/day range, in the 1960's the introduction of efficient single-stage centrifugal compressors made possible a new industry standard of 1 KMT per day. The new technology increased capacity and cut costs sharply and further expanded the market (See *Table I*).

**Table I: U.S. Nitrogen Production Trends  
KMT contained nitrogen\***

	<i>Capacity</i>	<i>Production</i>
1989	13136 <sup>b</sup>	12606 <sup>a</sup>
1985	12977 <sup>c</sup>	12965 <sup>a</sup>
1980	15501 <sup>d</sup>	14736 <sup>c</sup>
1975	13234 <sup>f</sup>	12346 <sup>e</sup>
1970	11916 <sup>h</sup>	10461 <sup>e</sup>
1960	4371 <sup>h</sup>	3628 <sup>g</sup>
1950	1420 <sup>h</sup>	1189 <sup>g</sup>
1945	1204 <sup>h</sup>	410 <sup>g</sup>
1939	340 <sup>h</sup>	244 <sup>g</sup>
1929	192 <sup>h</sup>	76 <sup>g</sup>
1919		28 <sup>g</sup>
1909		13 <sup>g</sup>
1899		1 <sup>g</sup>

\* Units differ in the original sources and have been converted. Sources as follows:

a. [MINYB 1989 Table 2, p.742]

b. [MINYB 1989 Table 4, p.744]

c. [MINYB 1985 Table 4, p.727]

d. [MINYB 1980 Table 4, p.601]

e. [MINFP 1985 Table 7, p.561]

f. [MINFP 1975 Table 1, p.750]

g. [HISSTAT 1975; Series P249+p250]

h. [HISSTAT 1975; Series P315]

There are several known processes for nitrogen fixation which are not currently exploited commercially. These include ionization and chemo-nuclear reactions to obtain oxides of nitrogen, fixation of nitrogen as metal nitrides or di-nitrogen complexes of transition metals, and reducing nitrogen bound up in certain transition metal complexes to ammonia. In addition, biological fixation by nitrogen-fixing microbes through genetic engineering is being developed for agricultural applications.

## Materials Balance for Nitrogen-based Chemicals

Virtually all nitrogenous chemicals are now manufactured from ammonia. Apparent U.S. consumption of ammonia in 1988 was 14.746 MMT (N-content), taking into account imports, exports and stock changes [MINYB 1989 p.741]. Of this amount, known domestic fertilizer use accounted for 9.536 MMT (N). However, a more detailed accounting by chemical suggests that 10.241 MMT (N) was used for domestic fertilizer purposes, or about 70% of apparent consumption. To confuse matters, 1.150 MMT (N) in the form of mono- and di-

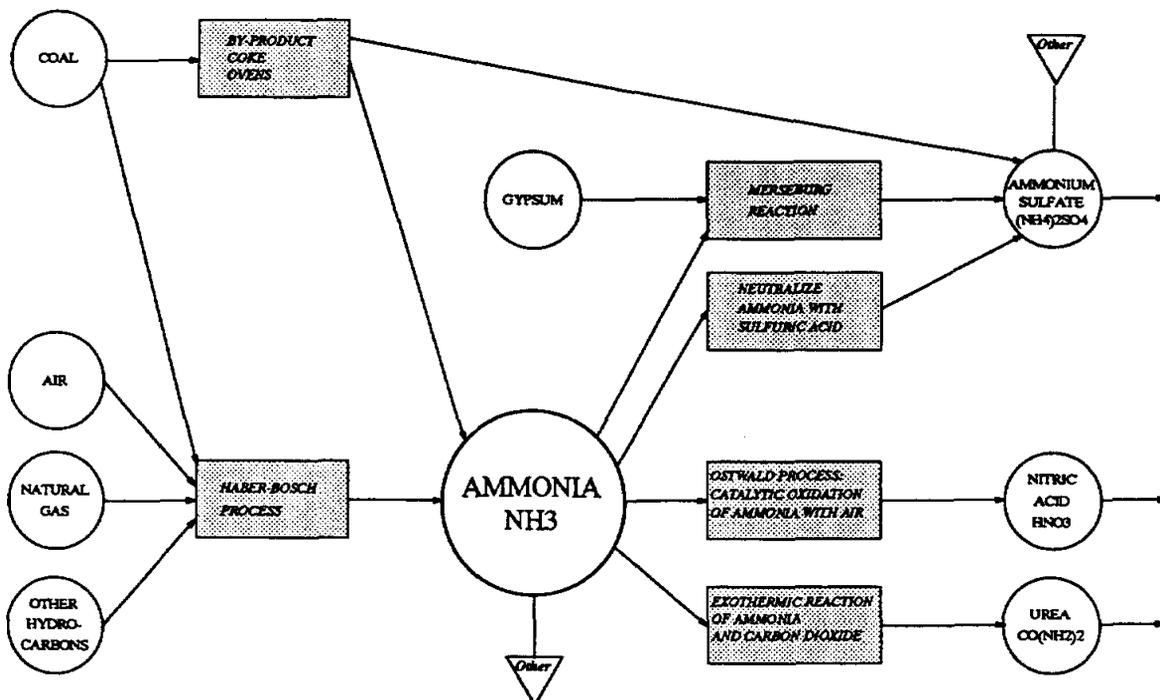


Figure 2: Production of Ammonia & Some Key Derivatives: Nitric Acid, Urea & Ammonia Sulfate

Source: [Ayres, Norberg et al 1989; Figure 5.1]

ammonium phosphates was produced and exported by the U.S. for fertilizer use outside the U.S. This presumably counts as part of "domestic consumption" for statistical purposes, and raises the fertilizer fraction to 77%. Fertilizers are spread on the land and is not normally counted as pollution, although nitrogenous fertilizers are known to contribute to nitrate pollution in ground waters.

Ammonia, as such, enjoys a significant share of the U.S. fertilizer market [3.422 MMT (N) is used in anhydrous form and 86 KMT (N) in aqueous solutions in 1988]. In addition, ammonia is used as a household cleaning agent, as an industrial refrigerant, in metallurgy, in pulp production, and in  $\text{NO}_x$  reduction equipment. These uses constitute a significant fraction of the "unaccounted for" fraction.

All other nitrogen chemicals (including the two most important, nitric acid and urea) are ultimately derived from ammonia. Ammonia, nitric acid and ammonium compounds are classed in SIC 28731. Ammonium and diammonium phosphates are among the most important fertilizers. U.S. production in 1988 was 2.350 MMT, of which 1.20 MMT was consumed domestically.

Nitric acid production in 1988 was 1.611 MMT (N) [CEN 1992]. About 5% of the ammonia input is lost in production, so 1.690 MMT (N) of ammonia was used. The nitric acid, in turn is used mostly to produce ammonium nitrate; 1.191 MMT (N) was used for this purpose in

1988, along with an equal amount of ammonia. Most of the ammonium nitrate was used as fertilizer (1.795 MMT (N), while the remainder — 587 KMT (N) — was almost exclusively used as an industrial explosive in the mining sector [MINYB 1989 p.745].

Other industrial uses of nitric acid amounted to 420 KMT (N) according to the Bureau of Mines [MINYB 1989 p.745]. Such uses include the manufacture of military explosives (other than ammonium nitrate), nitrobenzene, nitrocellulose, other "nitro" compounds (such as dinitrotoluene used in the manufacture of isocyanates) and steel pickling. Nitrobenzene, used entirely in the manufacture of aniline, for the dye industry, alone accounts for 5.2% of U.S. benzene consumption; based on 1988 benzene use data this implies 68 KMT (N) [IEI 1991], but a probable nitric acid requirement of 75 KMT (N). We also estimate that 0.080 MMT (N) was consumed in the production of dinitrotoluene for the manufacture of toluene diisocyanate (below), of which 60 KMT (N) remained in the product. Nitric acid is used as an oxidant in the production of adipic acid, probably accounting for 60 KMT (N) (below). We somewhat arbitrarily assign 100 KMT of nitric acid to military use, leaving 105 KMT for all other uses, including steel pickling and metal treatment.

Nitric acid is used as an oxidant in some chemical reactions, notably adipic acid (a nylon 66 precursor). To manufacture 1 kg of adipic acid from either cyclohexane or phenol (the main routes in the U.S.) requires 0.37 kg of nitric acid ( $\text{HNO}_3$ ). Adipic acid production for 1989 was reported as 744 KMT [CEN 1990, cited by Thiemens & Trogler 1991]. This implies total  $\text{HNO}_3$  consumption (as N) of 60 KMT. More than half of the nitrogen seems to be converted into nitrous oxide ( $\text{N}_2\text{O}$ ) as a waste [Thiemens & Trogler 1991]. Hence adipic acid production may contribute significantly to the atmospheric buildup of nitrous oxide, a greenhouse gas with a long atmospheric residence-time.

Total nylon production in 1988 was 1.466 MMT [CEN 1992]; the total for nylon 6 and nylon 6,6 together was 1.090 MMT, the remainder (nylon tape) consisting mostly of other polyamides (see *Figure 3*). Subtracting 566 KMT for nylon 6 leaves 534 KMT as the output of nylon 6,6 and 476 KMT for other polyamide resins. Nylon 6,6 is a co-polymer of adipic acid and hexamethylene diamine (HMD), with a kg of product requiring 0.65 kg of adipic acid plus 0.521 kg of HMDA [ANL 1980]. Thus, 534 KMT of nylon 6,6 would only require 331 KMT of adipic acid (direct) and 281 KMT of HMDA. This leaves 413 KMT (or 55%) to be accounted for.

We have no information on how much (if any) adipic acid may be used for other purposes. In 1974 "other uses", as plasticizers and polyol for polyurethanes, accounted for only 10% of output [Lowenheim & Moran 1975 p. 52]. One possible process, to manufacture HMDA via ammonylation, uses about 1.4 kg of adipic acid plus 0.33 kg of  $\text{NH}_3$ . If the 281 KMT of HMDA needed for nylon 6,6 were entirely derived from adipic acid by this route, most of the latter would be accounted for. This is unlikely, since other processes to make HMDA are certainly in use. However, there are also some other uses of HMDA (e.g. to produce hexamethylene di-isocyanate) as well as some other uses of adipic acid.

Urea production in 1988 was about 7.0 MMT (46% N-content), mostly for fertilizer — 3.311 (N) — and animal feed supplements (SIC 28732). About 46 KMT (212 KMT N-content) was used for industrial purposes [MINYB 1989 p. 745]. These were for amino-resins, urea-

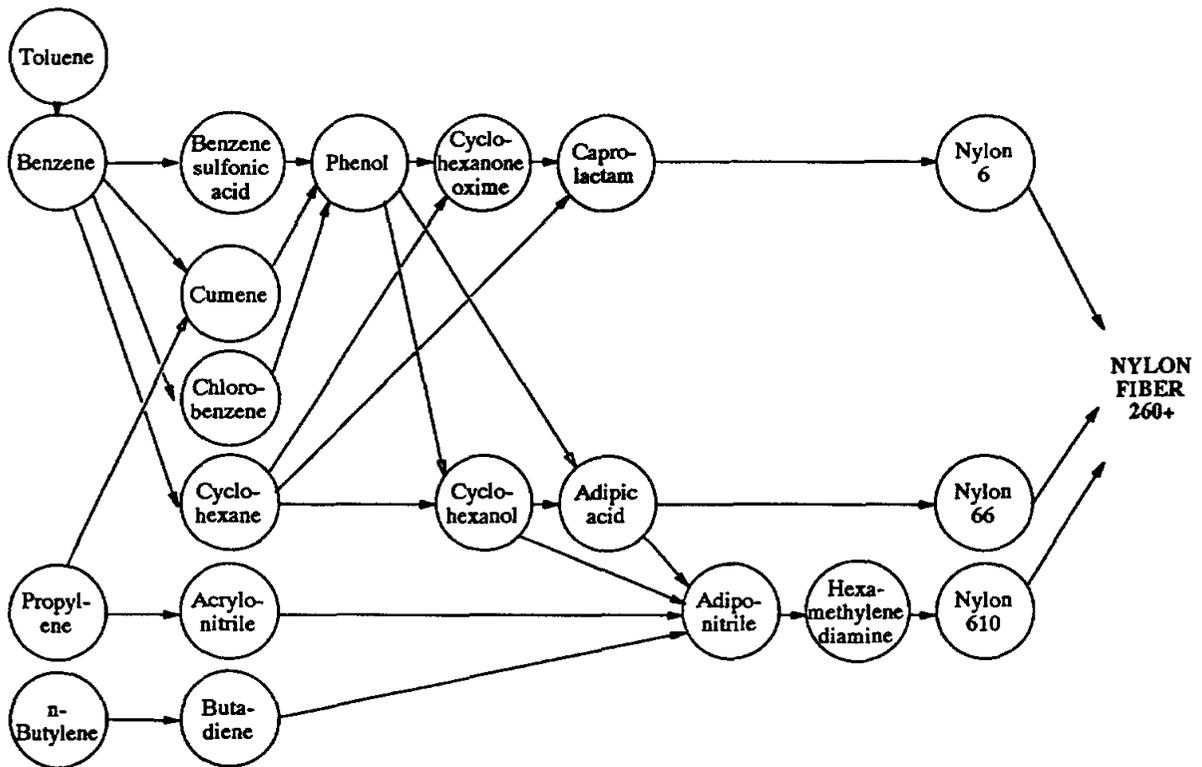


Figure 3: Steps in the Production of Nylon

Source: authors

formaldehyde (UF) and melamine. Total production of melamine resins in 1988 was 93 KMT [CEN 1992], or 62 KMT (N). Melamine is made by a complicated process (Stamcarbon) involving approximately 1.4 kg N-input (as urea) per kg melamine [Lowenheim & Moran 1975]. Incidentally, melamine production also consumes about 0.2 kg anhydrous ammonia per kg of melamine, or about 16 KMT (N). Thus, urea input to melamine must have been 130 KMT (N), with part of the difference of 68 KMT (N) being recycled as aqueous ammonia (84 KMT N) consumed as fertilizer [MINYB 1989 p.746]. U.S. production of urea-formaldehyde resin in 1988 was 0.646 MMT. UF resin is a straightforward condensation polymer in which the urea is entirely embodied in the product, which has 26% N-content. On this basis UF production accounted for 168 KMT (N). The two resins together embodied 230 KMT (N), disregarding losses and by-products; this is slightly larger than the figure reported by the Bureau of Mines for "industrial use" of urea (212 KMT N) [MINYB 1989 p.745].

Another important N-chemical is caprolactam, an intermediate in nylon 6 production. (In fact, the nylon is a straightforward polymer of caprolactam, so it contains all of the nitrogen in the monomer. Although nylon 6 output is not separately published, we can conclude that it must have been very close to the weight of caprolactam, or about 566 KMT.) The nitrogen content of U.S. caprolactam output in 1988 was 68 KMT (N) [MINYB 1989 p. 745]. There are several production processes in use, but the most common in the U.S. begin with cyclohexane or phenol. Based on the major process in use a few years ago, about 0.62 kg of ammonia is consumed, and 1.7 kg or ammonium sulfate is produced per kg of caprolactam. The ratio of nitrogen embodied in ammonium sulfate to nitrogen embodied in caprolactam is slightly less

than 3:1, while the ratio of input nitrogen in ammonia to nitrogen in caprolactam is almost exactly 4:1. On this basis, 68 KMT (N) in caprolactam — ultimately in nylon 6 — requires 272 KMT of nitrogen in ammonia and yields about 200 KMT (N) as ammonium sulfate, plus a some dilute nitric acid and wastes.

Based on the above calculation, we can account for 87 KMT (N) of ammonium sulfate as by-products of caprolactam and methyl methacrylate production, plus 50 KMT (N) as by-products of coke ovens, out of a total U.S. ammonium sulfate output in 1988 of 498 KMT (N) [MINYB 1989 p.745], leaving 161 KMT (N) as imputed primary production from ammonia and sulfuric acid. It happens that 243 KMT of sulfuric acid (100%) was consumed in the manufacture of nitrogenous fertilizers in 1988 [MINYB 1989 p. 1034]. Assuming all of this was used to make ammonium sulfate, it would only account for 69 KMT (N) as ammonia, leaving a shortage of 92 KMT (N) that must have been obtained from by-products from other industrial processes. Actually, one possible candidate is caprolactam, since there is at least one newer process that yields a 40% higher ratio of ammonium sulfate to caprolactam. Consequently, we assume this process has supplanted the older one, adding an additional 8 KMT (N) to the by-product supply. This would account for most of the missing by-product source. The remaining discrepancies are probably statistical.

Hydrogen cyanide HCN is another major nitrogen chemical intermediate. U.S. production in 1988 was 282 KMT (N), of which 90% was used captively by producers [IEI 1991]. Of this, 110 KMT (N) was apparently used in the manufacture of adiponitrile, an intermediate in the production of hexamethylene diamine used, in turn, to manufacture nylon 6,6 Unfortunately, HMDA cannot account for all of the adiponitrile (see above). We cannot reconcile this discrepancy..

According to one source 87 KMT (N) of HCN was consumed in 1988 in the production of methyl methacrylate, via the acetone cyanohydrin process [IEI 1991]. Another source reported 1990 cyanohydrin production in the U.S. as 610 KMT or 100 KMT (N). The two figures are reasonably consistent, bearing in mind that they do not refer to the same year. Methyl methacrylate is the most important acrylic monomer, used to manufacture "plexiglass", "lucite" and acrylic latex paints. As it happens, none of the nitrogen is embodied in the monomer or the polymer; it is almost entirely converted to ammonium sulfate, used as a fertilizer. All other uses of HCN (28% of production, or 85 KMT (N), are converted into sodium cyanide [18% or 51 KMT (N)] or miscellaneous chemicals. Of the sodium cyanide, 62% or 0.031 MMT (N), was used in the mining industry, mostly for the extraction of gold from ores. The rest of the sodium cyanide was used for electroplating or metal treatment.

It is noteworthy that HCN is a co-product of vinyl cyanide, better known as acrylonitrile (ACN), one of the major nitrogen chemicals, accounting for 308 KMT (N), in 1988 [MINYB 1989 p. 745]. There is only one process for ACN, the ammoxidation of propylene, which consumes 0.46 kg of ammonia and generates about 0.11 kg of HCN per kg of ACN. This process therefore consumed roughly 443 KMT of ammonia and produced 65 KMT (N) HCN as a by-product. The process also generated other by-products and wastes containing 0.070 MMT (N), partly consisting of acetonitrile, which is potentially recoverable but not very valuable. Working back, it appears that the N-content of ammonia consumed directly for HCN production would have been  $(282 - 65) = 217$  KMT (N).

ACN is an alternate source of adiponitrile; it is also used directly to make ABS (ACN-butadiene-styrene) rubber, SAN (styrene-ACN), nitrile rubber and acrylic fibers. If no ACN was converted into adiponitrile in 1988, a maximum of 308 KMT (N) was embodied in polymers, disregarding process losses.

Toluene diisocyanate is the other major N-containing intermediate in the manufacture of plastics and synthetic fibers. In 1988 this chemical accounted for 10.4% of all toluene output [IEI 1991], or 215 KMT of toluene. The toluene diisocyanate molecule substitutes two NCO radicals for two of the H atoms on the benzene ring. The conversion sequence is



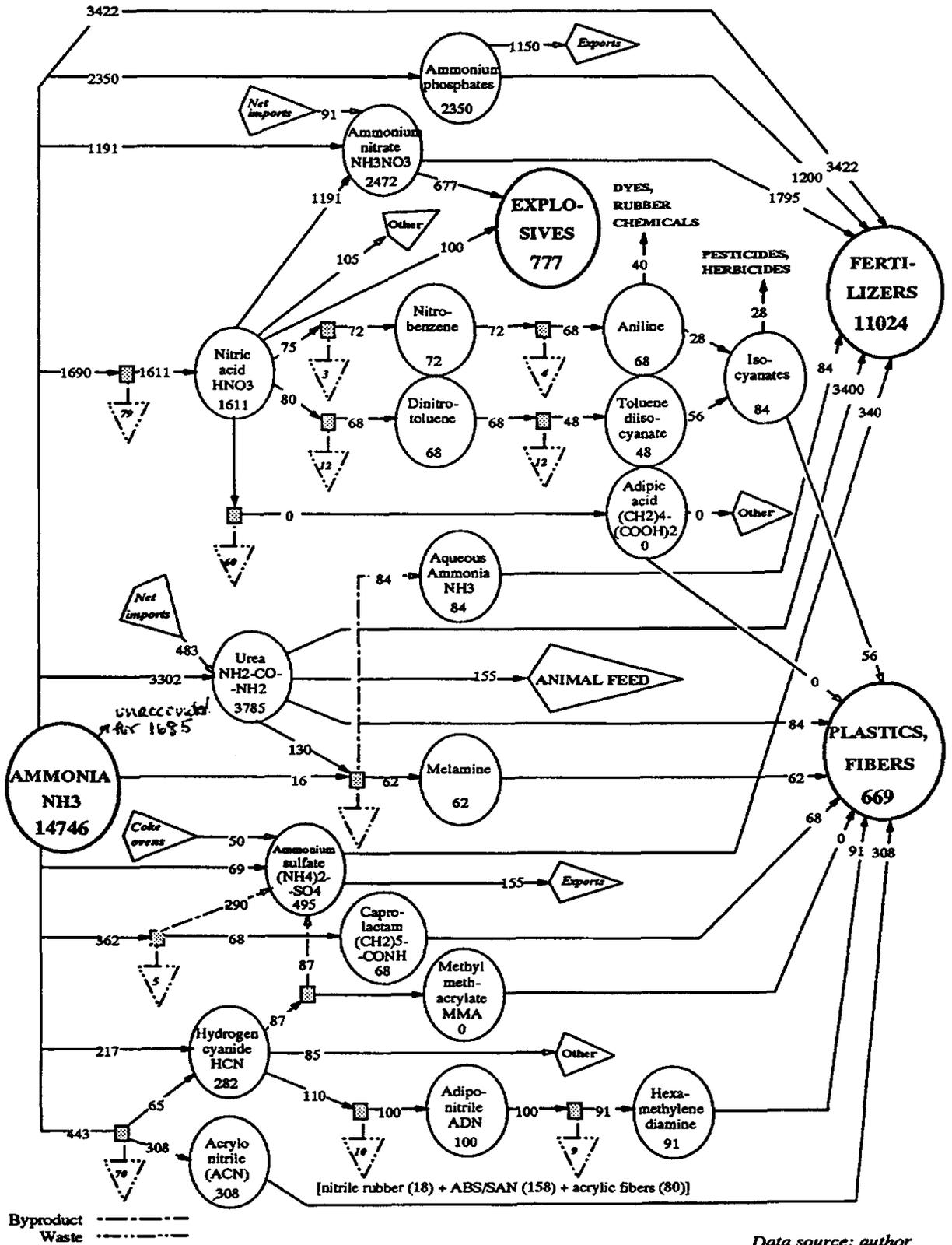
The overall yield is probably around 80%. There is no published information on the production of dinitrotoluene, but it is certainly a direct reaction with nitric acid, as noted above. The nitrogen embodied in toluene diisocyanate can be estimated on the basis of molecular weights (28 units of N per 92 units of toluene input), or 56 KMT (N) embodied in the product. This would have required at least 60 KMT (N) as nitric acid, assuming minor losses in the process.

A partial materials balance of the N-chemicals, accounting for 13.144 MMT (N), or about 89% of total ammonia supply, is shown in *Figure 4*. In fact, apparent 1988 U.S. consumption of ammonia (in terms of contained nitrogen) was 14.746 MMT. In addition, there were net imports of about 520 KMT (N) of N-chemicals (excluding the ammonium phosphates). We can account for over 90% of the total, but with some uncertainties.

Our total of 13.144 MT does not include chemicals for which we have no recent data, such as amides, alkyl amines, ethanolamines, nitro-paraffins, acrylates, ammonium chloride, hydrazine, ethylene diamine and hexamethylene tetramine, nor does it include household uses of ammonia, or uses of ammonia in other sectors (such as pulp and paper). For 1990 it was reported that approximately 4.73 MMT of "nitrogenous compounds" was produced in the U.S.; the major sub-categories were "amides" 139 KMT, "amines" 897 KMT, ethanolamines 330 KMT, "nitriles" (including acrylonitrile and acetone cyanohydrin), unreported, and "all other" 1.515 MMT. We can estimate the total for nitriles as roughly 1.835 MMT (by subtraction). Caprolactam is technically an amine (oxyhexamethyleneamine), and should be included in this total, although it is not listed separately for unknown reasons. The same is true of hexamethylene diamine (HMD). Because so much data is withheld, we cannot account for specific uses of nitrogenous chemicals beyond the foregoing. However, it would appear that at least 3 MMT of nitrogenous organic chemicals are not included in our listing. Assuming 10% N-content, on average, would not be unreasonable. This would account for another 300 KMT of N-content with a probably uncertainty of 100 KMT (N).

Our total does include identifiable losses in production amounting to 234 KMT (N). This is certainly an underestimate, however, since we have neglected the large number of products made in small quantities via batch reactions that are considerably less efficient than the large-scale continuous processes. Our best guess is that process losses (unreacted feedstocks or contaminants) amount to at least 3% of the total, or 450 KMT. Thus, to a reasonably good approximation, we have accounted for 95% of the synthetic fixed nitrogen produced and consumed in the U.S. in 1988.

Industrial Metabolism of Nitrogen



Data source: author

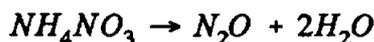
Figure 4: Materials Balance of Ammonia-based Chemical Production in the U.S. 1988 (1000 MT N-content)

It is difficult to estimate chemical process wastes with any precision due to the uncertainty about ammonium sulfate. The following (in thousands of metric tons N) is our best estimate, based on taking differences between published input N requirements and N embodied in products:

HNO <sub>3</sub> production (5% loss):	79
Adipic acid production:	30
Acrylonitrile production:	70
Caprolactam:	5
Toluene di-isocyanate:	12
Others:	38
Subtotal of the above:	234

It is of some interest that the major waste streams from nitric acid and adipic acid manufacturing are in the form of NO, while a significant fraction of the latter, at least, takes the form of nitrous oxide N<sub>2</sub>O, one of the more potent "greenhouse" gases. It has been suggested that the N<sub>2</sub>O emissions from adipic acid manufacturing is nearly equal to the quantity of product [Thiemens & Trogler 1991]. However, process data suggests that the maximum output of N<sub>2</sub>O from adipic acid manufacturing (even assuming 100% conversion of 60 KMT N to N<sub>2</sub>O) would be around 94 KMT. However a 50% conversion rate is more plausible.

We have not been able to determine the reaction products of nitrate explosives such as ammonium nitrate. It is not clear how complete the oxidation of nitrogen would be under non-equilibrium conditions. However, it is interesting to note that an old commercial process for producing nitrous oxide (laughing gas) has the simple formula:



It would not be surprising if use of ammonium nitrate as an explosive generated significant quantities of N<sub>2</sub>O. A straightforward estimate of the reaction products of ammonium nitrate decomposition suggests that as much as 9% of the N-content could be converted to N<sub>2</sub>O [Axtell 1993]. Assuming 777 KMT (N-content) of nitrate explosives, mainly ammonium nitrate, this suggests that 110 KMT of N<sub>2</sub>O might be generated by explosives.

## Agricultural Uses and Losses of Nitrogen

As mentioned in the opening paragraph, nitrogen is an essential element for protein production. It can only be ingested (by plants) as soluble ammonium (NH<sub>4</sub><sup>+</sup>) ions, nitrate (NO<sub>3</sub><sup>-</sup>) ions, or soluble organic molecules such as amino acids. There are many routes by which soluble nitrogen finds its way into the soil.

Nitrogen oxides are created in the air either by electric storms or fuel combustion. These oxides then react with water vapor and create nitrous or nitric acid (HNO<sub>3</sub>) which falls as a

component of acid rain. Nitric acid subsequently reacts with metallic salts to form nitrates. Ammonia is also emitted by volcanoes.

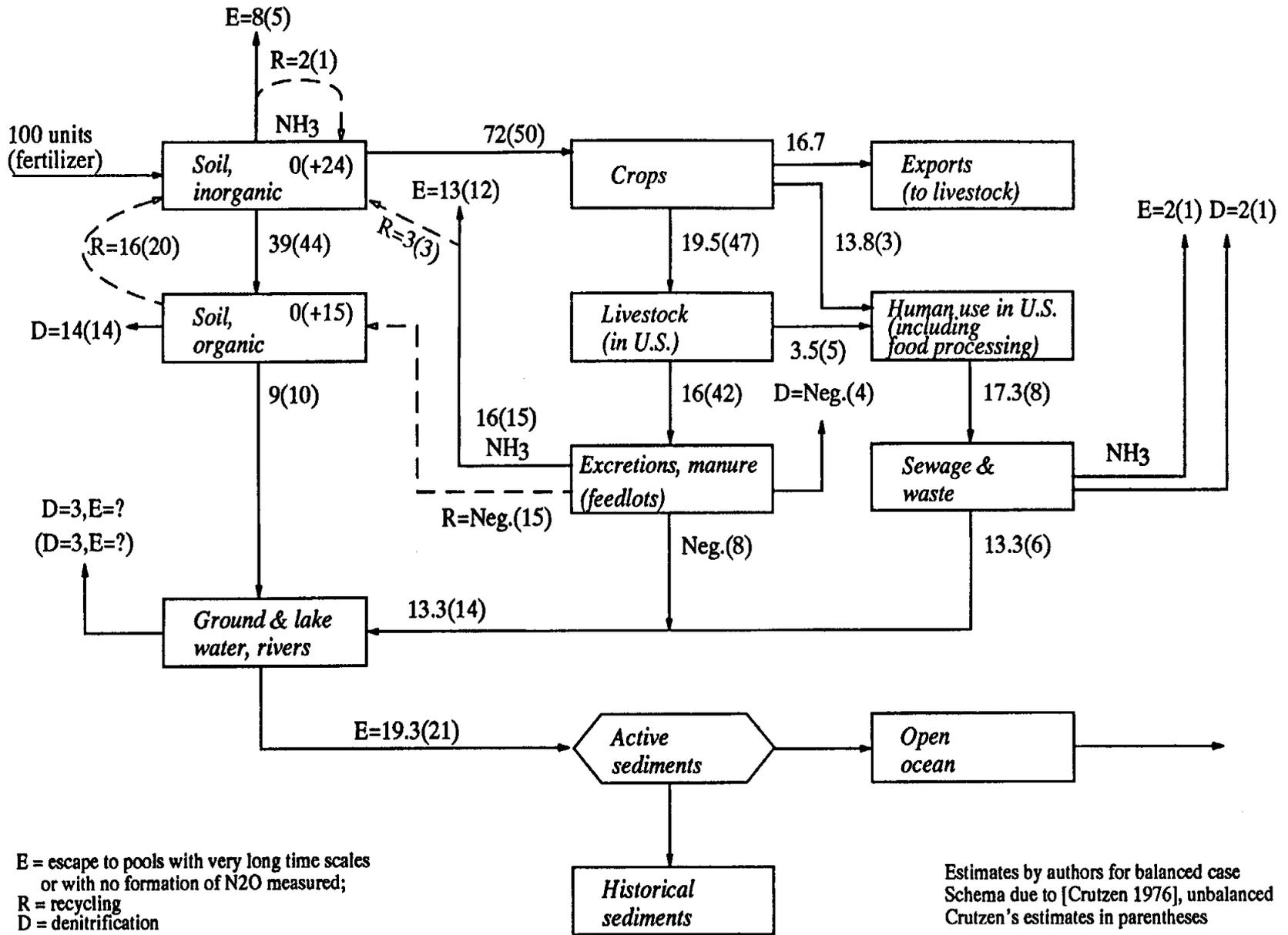
Rhizobia bacteria in the root nodules of legumes (such as soybeans) are able to fix nitrogen from the air. Some other varieties of bacteria can also fix nitrogen. A third source - from a practical point of view - is the recycling of plant and animal matter. Some of this nitrogen from decaying organic matter is released in the form of ammonia ( $\text{NH}_3$ ), and, along with ammonia from anthropogenic sources, is returned to the soil in rain.

For centuries nitrogen fixation by atmospheric electrical discharges, from legumes and from decayed matter (manure) were the only means of restoring lost fertility to soil. Gradually, the recycling process was accelerated through composting and distribution. Organic matter in the soil may contain as much as 5-6% nitrogen, but this is not available to plants until it has been released by bacteria or fungi in the form of ammonia or nitrates. Soils with plentiful organic matter can retain much of this for future use by plants.

With increasing pressure on farmers to increase crop yields the available nitrogen in the soil was used more rapidly than it could be replaced by the available plant and animal materials. In 1930 the annual nitrogen deficit for the U.S. was estimated at 3.4 million tonnes, despite some use of nitrogen fertilizers [Shreve 1956, p. 397]. However, fertilizer use has increased very rapidly since then. In recent years a growing proportion of nitrogen has been applied by direct injection of anhydrous ammonia into the soil, particularly in the large farms of the Mississippi valley. However, the major portion is still applied either in solid or liquid form that can be handled more easily and applied in combination with other plant nutrient materials.

Crutzen has estimated the partitioning of 100 units of agricultural fertilizer into ultimate sinks as follows [Crutzen 1976, cited in USNAS 1978]: (1) accumulation in the soil, groundwater or sediments: 38 units; (2) active recycling through the soil-biosphere system as manure or plant residues: 39 units; (3) denitrification to  $\text{N}_2$  or  $\text{N}_2\text{O}$  which return to the atmosphere: 23 units. In this picture about 17 units escape as ammonia, 4 from the point of fertilizer application, 12 from manure and 1 from sewage. Another 6 units escape as  $\text{N}_2$  (5.6 units) or  $\text{N}_2\text{O}$  (0.4 units). Crops initially take up 50% (50 units) of the N-content of the fertilizer; of this 47 units are consumed by livestock, and 42 units end up in manure and animal urine, of which 15 units go back to the soil, along with 30 units of nitrogen from plant residues and 4 units from local deposition of gaseous emissions. But, during each cycle, 10 units of organic N are lost to waterways and ground water, so the amount of organic N "permanently" added (i.e. for the next cycle) is 15 units, while 24 units of inorganic N are also added for the next cycle. This represents accumulation within the terrestrial biosphere and cultivated lands. Crutzen's allocation neglects NO emissions from soil, which are not well documented, but known to be significant (see below).

Our own estimates differ significantly from Crutzen's, because we assume a balanced system, (with no net gain or loss by the soil) as shown in *Figure 5* below. Also, we have modified Crutzen's figures with respect to uptake by animals and human consumption.



Estimates by authors for balanced case  
 Schema due to [Crutzen 1976], unbalanced  
 Crutzen's estimates in parentheses

Figure 5: Partition of 100 Arbitrary Units of Fixed Nitrogen in U.S. Agriculture

Of the 50% of nitrogen in fertilizer not taken up by the harvestable parts of plants and removed in crops, a small amount (possibly 10%) is lost immediately to runoff or ground water. A considerable part (Crutzen estimates 30%, which we accept for purposes of discussion) returns to the soil in organic root, stem or leaf material that gradually decays. Some of the fertilizer and some of the organic material is, in turn, converted to  $N_2$  (or  $N_2O$ ) by denitrifying bacteria: Crutzen estimates 15%, which is consistent with other data (see below).

In well ventilated soils having low organic matter (with a carbon/nitrogen ratio of less than 15) when the quantity of ammonium ions exceeds the absorption by plants and microbes the excess ammonia is oxidized to nitrates by a nitrification process. The first step (to nitrite) is brought about by bacteria such as *nitrosomas*. The second step (to nitrate) is carried out by other bacteria such as *nitrobacter*. These nitrates remain in the soil for plant use, up to certain limits depending on temperature, etc. Most nitrate compounds are soluble and can be leached from the soil — particularly in permeable soils having low organic matter and high rainfall. However, in soils with high levels of decaying organic matter, air circulation, and a high microbial population, the microbes consume the nitrogen in the form of ammonia and effectively store it in their body-mass for future use by plants — resulting in very little loss by leaching.

Bacterial action also continuously removes organic nitrogen from soils altogether by converting organic nitrogen to volatile  $NH_3$ , some of which escapes into the atmosphere. However denitrification is the dominant process. In clogged soils having insufficient air circulation, fertilizer nitrates may be denitrified (reduced to gaseous nitrogen) by anaerobic microbes which break up the molecules to satisfy their demand for oxygen. Crutzen's estimate was 6% direct loss by denitrification at the point of application and another 9% from subsequent decay of organic materials.

Bacteria in the soil convert nitrates to di-nitrogen ( $N_2$ ) and nitrous oxide ( $N_2O$ ) in a ratio of about 16:1. The ratio is highly variable, and depends strongly on local conditions. Fertilizer use is, however, reckoned to be one of the major sources of atmospheric  $N_2O$  emissions, accounting for roughly 1.5 MMT globally in 1988 [USNRC 1992]. U.S. fertilizer use is approximately 1/6 of the world total, which implies U.S.  $N_2O$  emissions of around 250 KMT, or 160 KMT (N) in 1988. Based on the 16:1 ratio, this suggests total  $N_2$  emissions of the order of 2.56 MMT. If all of this were attributed to agricultural (i.e. fertilized) land it would amount to about 23% of input fertilizer (N content). However, it seems more realistic to allow for a significant non-agricultural contribution. This is consistent with Crutzen's estimate of 15%, divided 13.1% as  $N_2$ , 0.9%  $N_2O$  and the rest as  $NO$ .<sup>4</sup>

The rest of the applied fertilizer not otherwise taken into account returns to the atmosphere directly as ammonia. Ammonia emissions depend on fertilizer type. In the case of urea, the ammonia emission factor is apparently about 0.2 (20%); for ammonium sulfate it is 0.1

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<sup>4</sup> Recent evidence suggests that significant quantities of  $NO$  are also produced by soil bacteria, especially from fertilized agricultural land. Annual emissions from U.S. cropland were estimated to be 208.5 KMT (or 97 KMT N-content), of which 136 KMT were attributed to corn alone [Williams *et al* 1992, Table 4]. Thus  $NO$  emissions account for about 0.9 % of applied N.

(10%); for other fertilizers — including anhydrous  $\text{NH}_3$  injected directly into the soil — it is about 0.03 [Schlesinger & Hartley 1992, Table 6]. In 1988 urea fertilizer use in the U.S. was 3.4 MMT (N) and ammonium sulfate fertilizer use was 0.340 MMT. On this basis, direct ammonia emissions to the atmosphere from would have been close to 1 MMT (N). Direct emissions of ammonia would seem to account for about 9% of total N-content of applied fertilizer or 18% of the nitrogen not embodied in harvested crops. On the other hand, Crutzen estimates that about 20% of ammonia emissions (including emissions from animal excreta) are re-deposited on agricultural soils. We accept this estimate, although it might be too low.

However, we now have accounted for 105 units of input (including the 5 units of ammonia redeposition) and  $50 + 24 + 10 = 84$  units of output from the land, including harvested crops. This particular combination implies that  $105 - 84 = 21$  additional units of organic N are removed from the land surface by grazing animals, permanently immobilized in some manner, or find their way to groundwater or waterways. If 30 units are left on the land as unharvested biomass (as Crutzen assumed), the difference between what is left behind after harvesting and what is removed ( $30 - 21 = 9$  units) must be organic nitrogen uptake from the soil. This seems relatively small compared to the 30 units of organic N added to the soil in the form of crop detritus.

This picture is not really satisfactory, since 14 of the 15 units to denitrification start from organic materials. To balance inputs and outputs to the organic component or soil alone (excluding crop biomass), we have 30 units of annual increment, of which 9 goes back to plants and 14 is consumed by denitrifying bacteria, leaving only 7 units lost to other processes. This seems more reasonable, but it leaves 14 surplus units of inorganic N to account for. If the figures for crop removal (50 units) and loss to ammonia volatilization are correct, the only way to balance the system is to assume that 24 units of *inorganic* N are lost to ground water and/or surface waters, or otherwise immobilized. This seems excessive.

Following this line of reasoning, one is forced to conclude that — in a balanced system — crop removals must be larger than 50%. (In other words, Crutzen was considering a system in which nitrogen was accumulating in the soil, presumably to compensate for prior deficits). Indeed, we have seen estimates that nitrogen uptake by crops in the U.S. during the early 1970's was in the range of 64-80% (depending on the year) with an average of 72%. The two cases are compared roughly in *Figure 5*. The main differences are (1) that Crutzen did not break out exports (2) our estimates of the N-content of animal feed and food for human consumption differ considerably from his and (3) we believe there is virtually no return of nitrogen from animal wastes from feedlots to the soil, contrary to Crutzen's assumptions.

Harvested output of field crops in 1988 was 416.3 MMT (exclusive of harvested roughage fed to animals), of which 139.3 MMT was exported and the remainder — 277 MMT — consumed directly or indirectly within the U.S. There were no significant imports of raw products in this category. Indirect consumption (as animal feed) accounted for most of the difference. Final *direct* human consumption of foodstuffs derived from field crops (flour, sugar, vegetable oils, potatoes, beans) amounted to 31.81 MMT.

According to the US Department of Agriculture [USDA 1992, chapters I, VI], livestock in the U.S. in 1988 were fed 119.4 MMT of feed grains, plus 3.7 MMT of food grains (mostly wheat). Other harvested animal feeds included 123 MMT of hay and alfalfa, 4.76 MMT of

sorghum as silage, and approximately 68 MMT of harvested roughage (such as cornstalks) mixed with other feeds, for a total of 319 MMT harvested inputs. By-products of the food processing industry such as grain mill by-products, oilseed meal, meat and fish meal, dried milk and molasses accounted for an additional 38.9 MMT. Thus, animals consumed 162 MMT of the 272 MMT of harvested crops consumed in the U.S. (Grazing animals also consumed 200 MMT of pasturage and 68 MMT of harvested roughage, such as cornstalks.)

Animal wastes are a major pollution problem, especially in the vicinity of animal feed lots and large scale poultry producers. Per capita annual  $\text{NH}_3$  emissions from animal metabolism have been estimated as follows: 15.5 kg for cattle and horses; 2.4 kg from sheep, 2.35 kg from pigs and 0.21 kg from (average) chickens and turkeys [Schlesinger & Hartley 1992, Table 4]. Populations of these animals in the U.S. for 1988 were 99.6 million (cattle), 55.5 million (pigs), 10.9 million sheep and lambs and 5.7 billion chickens (including broilers) and turkeys. This implies total  $\text{NH}_3$  emissions from animals of 2.91 MMT, or 2.4 MMT (N), of which at least three fourths, or 1.8 MMT (N) would have been emitted at feeding stations or feedlots in the U.S.

If 50% of the nitrogen content of fertilizer is taken up by field crops, as USDA contends, then one would have to assume that 5.75 MMT (N content) was removed with the harvest. Of this, 33.4% or 1.91 MMT was exported, 27.6% or 1.59 MMT was processed for human consumption in the U.S., and the rest (39 % or 2.25 MMT) was consumed by animals. A significant fraction of this was used for animal metabolism. The animal products, in turn, were converted into human food, mostly for domestic consumption. So, presumably,  $2.25 + 1.91 = 3.84$  MMT (N) entered the human food chain within the U.S.

The average per capita food consumption comes to about 450 kg retail weight per year (exclusive of water content of fresh milk and fruit juices). While many foods have above average protein (meat, milk and eggs) and other little or none (e.g. sugar), average nitrogen content is at least 2% (equal to the average of harvested crops), or 20 pounds per capita per year. Nationally, this amounts to 2.25 MMT (N), which is only a small fraction of the total nitrogen input to domestic fertilizer, 11.2 MMT (N).

The work of Schlesinger and Hartley, cited above, suggests that nitrogen lost (as urine) at feeding stations and feedlots, where most harvested animal feeds are consumed, was probably close to 1.8 MMT, or 16% of fertilizer N. The bulk of this was volatilized directly into the atmosphere as  $\text{NH}_3$ , although some gets into ground water. Assuming the urine accounts for 1.8 MMT (N), unprocessed animal products destined for human consumption probably embodied  $(2.25 - 1.8) = 0.45$  MMT or 450 KMT (N). There is little loss *en route* to the table for dairy products, but a considerable fraction of the average animal carcass is converted to other uses, recycled as feed, or discarded as waste. Of this, a significant fraction consists of hooves, hides, wool, feathers, and ligaments, which are nearly pure protein and consequently nitrogen rich. We estimate this loss (or diversion) as 50 KMT (N), leaving about 400 KMT in meat and dairy products actually consumed.

Bearing in mind our calculation that food products contain 2.25 MMT (N), the above implies that about 1.8 MMT (N) in food is incorporated in proteins of vegetable origin. This is consistent with 1.91 MMT (N) embodied in raw products if we assume that nitrogen lost or

diverted in food processing — mostly grain milling — operations accounts for 0.11 MMT or 110 KMT (N). Most of the latter is probably converted to animal feeds. The 2.25 MMT (N) in human food (in the U.S.) was almost entirely discharged either to sewage systems and thence to rivers and streams, or to septic fields and thence to ground water.

It is worth mentioning that most of the crops exported by the U.S. are fed to animals in other countries, where the ultimate fate of the nitrogen is similar to that in the U.S. livestock feeding sector. However the details of the nitrogen budget in a country that imports large quantities of animal feed (e.g. the Netherlands) will be somewhat different from the U.S. pattern, with greater proportional losses to sewage and waterways and less emissions to air due to fertilizer volatilization.

As noted previously, crop harvesting (and erosion) removed nitrogen from U.S. soils considerably faster than it was being replaced, probably until some time in the 1960's<sup>5</sup>. That net depletion process resulted in a substantial net flow of nitrogen from rural to urban areas (embodied in food products) from whence much of it was returned to the environment in sewage and/or garbage. Some other parts of the world, notably Africa, are still losing soil nitrogen from their soils faster than it is being replaced.

However, due to the rapid increase in nitrogen fertilizer use, runoff from agricultural areas is now the dominant source of aggregate nitrogen emissions to the water (and has been since the 1960's). In addition, large-scale animal feed lots have become major point sources of nitrogen emissions (both to water and air) by way of manure and urine<sup>6</sup>. In the extreme case of a heavily urbanized region, most N-emissions can evidently be attributed to food processing and consumption wastes (sewage).

## Emissions of Toxic Nitrogenous Chemicals

It is important to consider the ultimate fate of nitrogen-containing chemicals. It is reasonable to assume that most of them — especially the explosives — will ultimately be oxidized. When this occurs, the carbon and hydrogen are converted to carbon dioxide and water vapor, respectively, while the nitrogen goes to NO and NO<sub>2</sub> or, in some cases, N<sub>2</sub>O. However, there will undoubtedly be traces of ammonia, HCN, and other volatiles such as carcinogenic Peroxy-Acyl Nitrates (PAN), one of the intermediates produced by photolytic reactions between NO<sub>2</sub> and hydrocarbons in the atmosphere.

Cyanides are found in many industrial wastes, especially quench waters from coking operations and metal heat treating operations. Sodium and potassium cyanides are also used in both gold and silver mining, in the "heap leach" process to beneficiate low grade ores to the point where smelting is feasible. Cyanides are extremely toxic. The cyanide ion CN<sup>-</sup> is

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<sup>5</sup> When U.S. consumption of synthetic nitrogenous fertilizers presumably reached rough balance with annual removals by harvesting and erosion. It is interesting to note that the National Research Council estimates a net nitrogen buildup in soil and groundwater of the order of 1.5 million tonnes per year (1972) [USNAS 1978].

<sup>6</sup> Animal urine accounts for at least 50% of excreted nitrogen, in the form of urea. Under typical feedlot conditions urea is rapidly hydrolyzed to carbon dioxide and ammonia.

toxic to most fish at a level of 0.1 mg per liter (kg) of water, for instance. Fortunately, cyanides easily form metallic complexes, such as ferrous cyanide  $\text{Fe}(\text{CN})_2$ , ferric cyanide  $\text{Fe}(\text{CN})_3$ , ferro-cyanides, etc. These complexes are much less toxic. However, there is a possibility that complex cyanides could revert to the simpler forms under certain circumstances, such as increased acidity (lower pH), increased temperature, or UV radiation. This means that accumulations of metallic cyanide complexes in the surroundings of old gold and silver mining operations are still potential "chemical time bombs"<sup>7</sup>.

One of the most toxic and carcinogenic of all groups of compounds are the nitrosamines, characterized by the N-N=O linkage. It is known that amines, such as dimethylamine, can be nitrosated in the atmosphere, by reaction with nitrous acid vapor, in equilibrium with NO and  $\text{NO}_2$  to yield nitroso-dimethylamine. All the amines can apparently be nitrosated under appropriate conditions. It is believed that nitrosamines become active carcinogens after being decomposed by enzymes. Of the first 100 nitroso compounds studied, over 80 were carcinogenic in test animals, sometimes after a single dose.

These compounds were first detected in the environment in the mid-1970's. The first confirmed atmospheric detections were in Baltimore, in the vicinity of a plant that manufactures methyl amines and hydrazine. Other amine plants have subsequently been associated with atmospheric nitrosamine findings. Later research discovered nitrosamines in the expired air of rats that had been fed on amines and nitrates. There is some reason to suspect that rocket engine exhaust (from hydrazine) may also be a source of nitrosamines. There is also reason to think that nitrosamines can be formed in food, e.g. bacon, that has been preserved by nitrites. Nitrosamines are also found in tobacco smoke, and may be one of the cancer causing agents.

A few nitrosamines were manufactured, as such, in the 1970's, mainly for use as a retardant in the rubber industry. However amines have been produced in fairly large quantities for many years. Total U.S. amine production in 1972 was about 910 thousand metric tons (KMT). This included hexamethylene diamine, aniline, ethanolamine and melamine. For 1991, the totals for these compounds was 806 KMT, plus aniline and melamine (see *Figure 4*). The presence of these in the environment, in conjunction with  $\text{NO}_x$  seems to be conducive to the formation of nitrosamines.

## **Anthropogenic Sources and Emissions of Oxides of Nitrogen ( $\text{N}_2\text{O}$ , $\text{NO}_x$ )**

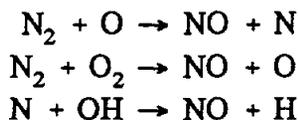
Oxides of nitrogen are formed naturally by electrical discharges in the atmosphere. They are also formed when either atmospheric or fuel-bound nitrogen are "burned" in air. This is the major anthropogenic contribution. The major nitrogen oxides are  $\text{N}_2\text{O}$ , NO and  $\text{NO}_2$ . In the absence of fuel-bound nitrogen, typically 95—98% of the  $\text{NO}_x$  in combustion exhaust gas consists of NO. Incompletely oxidized nitrogen is oxidized further to  $\text{NO}_2$  in the atmosphere.  $\text{NO}_2$  is eventually dissolved in water and precipitated as nitrous acid, or oxidized further to nitric acid. In either case it is a major contributor to acid rain and acidification of soils. In addition,  $\text{NO}_2$  reacts with hydrocarbons and oxygen (especially in the presence of UV

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<sup>7</sup> The terminology is due to [Stigliani 1988]

radiation) to form peroxy-acyl-nitrates (PAN), one of the most irritating and carcinogenic ingredients of urban smog.

The reaction chemistry for  $\text{NO}_x$  formation by fossil fuel combustion is not completely known, but the most probable sequence for thermal  $\text{NO}_x$  seems to be the following [Lim *et al* 1981].



where oxygen and hydrogen atom concentrations are in equilibrium.

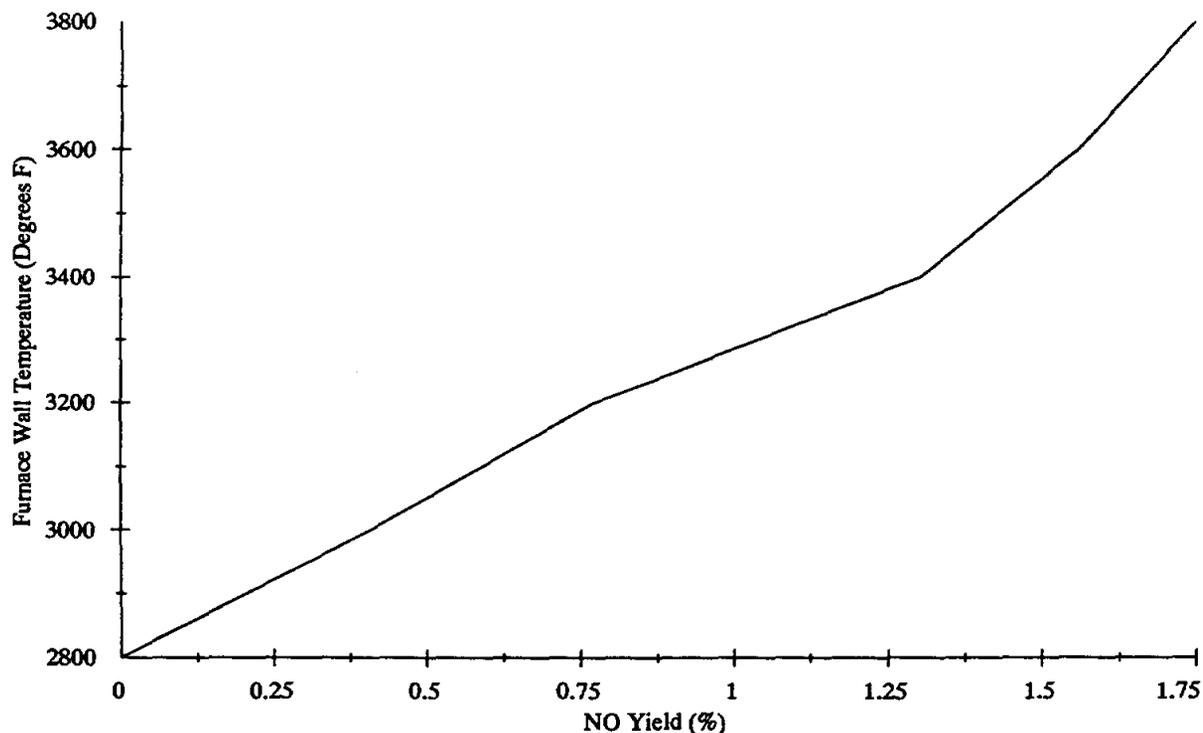
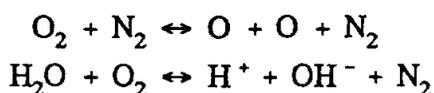


Figure 6:  $\text{NO}_x$  Formation vs. Temperature, Based on Measurements at Furnace Wall  
Source: [Ermenc 1956; cited in Engdahl 1968]

The reaction rate for  $\text{NO}_x$  formation is determined by two factors. The activation energy of the initial endothermic reaction step is quite large (317 KJ/mole) and probably determines the overall reaction rate. The reaction is, therefore, highly temperature dependent: equilibrium  $\text{NO}$  levels in heated mixtures of  $\text{N}_2$  and  $\text{O}_2$  at atmospheric pressure is an increasing function of temperature (Figure 6). The mathematical form  $e^{k/T}$ , where  $k$  is a constant, has been suggested [Mackinnon 1974]. More recent data for fluidized beds is shown in Figure 7.

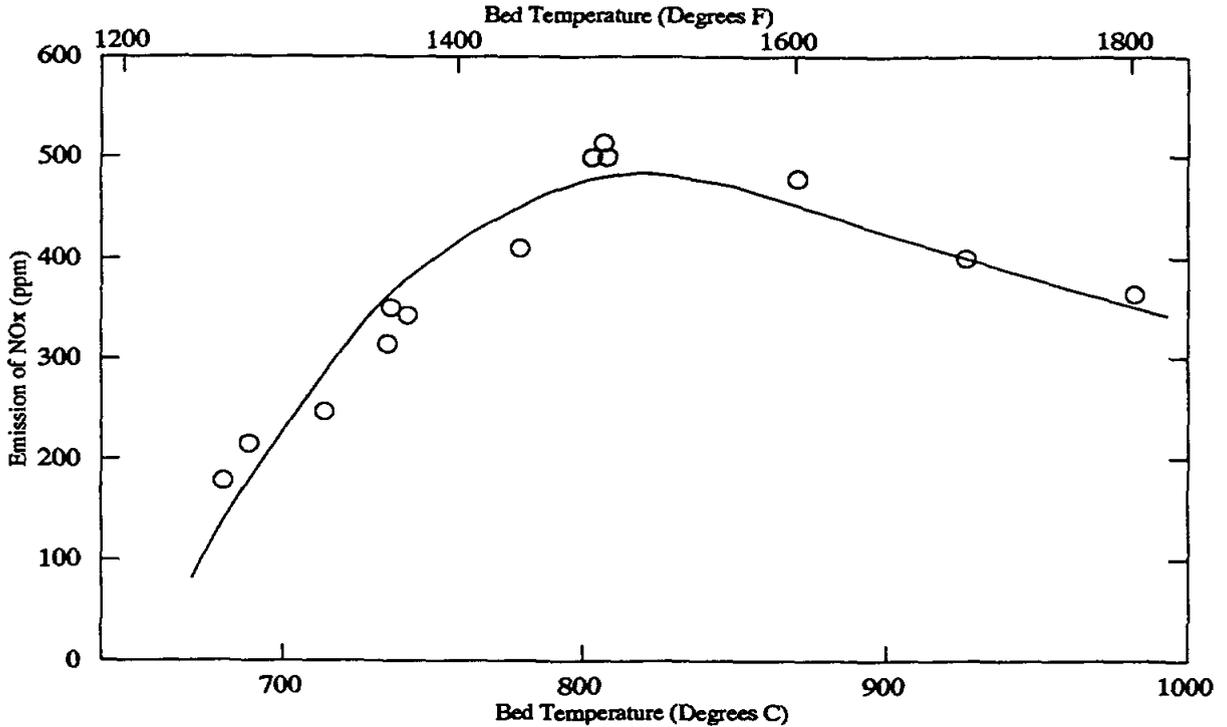


Figure 7: NO<sub>x</sub> vs. Bed Temperature, Equivalence Ratio 0.847 (18% excess air)  
 Source: [USEPA 1979-e]

Because of the high activation energy for the nitrogen oxidation reaction, it will only occur after all available carbonaceous fuels are exhausted. Thus, the rate of NO<sub>x</sub> production also depends on the amount of excess oxygen that is present beyond the stoichiometric air/fuel ratio (14.6 for the case of gasoline). The equilibrium NO level is also proportional to the product of N<sub>2</sub> concentration times the square root of O<sub>2</sub> concentration, times residence time in the flame. Because of these relationships, air/fuel ratio is a dominant factor in determining NO<sub>x</sub> emissions in the absence of fuel-bound nitrogen. Figure 8 shows typical NO<sub>x</sub> (NO, NO<sub>2</sub>) emissions as a function of air/fuel ratio for automobile gasoline engines [Jackson 1968].

For smoldering fires, or "rich" fuel air mixtures, NO<sub>x</sub> production is negligible. However for "lean" fuel air mixtures, it becomes increasingly significant. Thus, NO<sub>x</sub> is, for practical purposes, not significantly produced in low temperature combustion processes, except to the extent that fuel-bound (organic) nitrogen is present.

However, organic nitrogen is present in coal and residual oil and in biomass<sup>8</sup>. Thus, fuel-bound nitrogen in all organic materials, as well as in fossil fuels (in coal and residual oil) also contributes to both N<sub>2</sub>O and NO<sub>x</sub> emissions. Apparently N<sub>2</sub>O — one of the most potent "greenhouse gases" — is associated *only* with fuel-bound nitrogen.

<sup>8</sup> In coal the range is between 0.6% and 2% by weight (Figure 9). In terrestrial biomass, it has been found that the nitrogen/carbon molar ratio is fairly constant (1:80), which means that the C/N weight ratio is 68.5. This is about the same as the average ratio for coal.

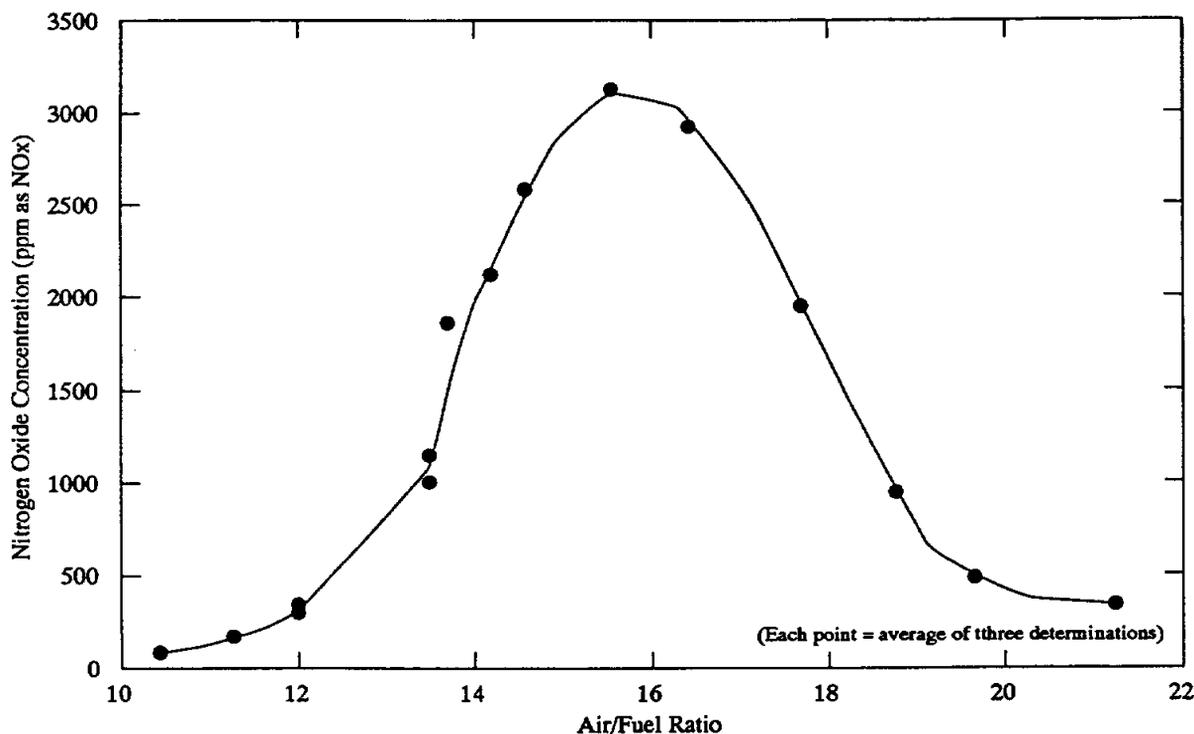


Figure 8: Influence of Air-Fuel Ratio on Concentration of NO<sub>x</sub> in Exhaust Gas

Source: [Adapted from Jackson 1968, Figure 5A]

Median nitrogen content of US coals corresponds to approximately 1350 Ng/J of NO<sub>2</sub>, assuming 100% conversion; the 25—75 percentile range is fairly narrow, viz. 1250—1400 Ng/J [Lim *et al* 1981]. Figure 9 shows measured relationships between coal nitrogen content in percent by weight and *measured* NO<sub>x</sub> emissions. The median NO<sub>x</sub> (as NO<sub>2</sub>) emission level is about 270 Ng/J. The 25—75 percentile range for bituminous coal combustion corresponds to NO<sub>x</sub> (as NO<sub>2</sub>) emissions in the range of 240—300 Ng/J [Lim *et al* 1981]. Based on this data, it appears that if there were thermal contribution to NO<sub>x</sub>, the average conversion fraction for fuel-bound nitrogen to NO<sub>x</sub> would be  $270/1350 = 0.2$ .

The relative contribution of fuel-bound nitrogen to NO<sub>x</sub> emissions from combustion is not yet completely understood. However studies have shown that the contribution of fuel bound N to total NO<sub>x</sub> may be as high as 50% for residual oil, and 80% for coal. Looking at it another way, 20%—90% fuel-bound nitrogen in oil and 10%—60% in coal may be converted to NO<sub>x</sub>, depending on conditions of combustion. No data on wood combustion is available.

Emissions vary widely according to the type of combustion equipment, so test data is limited and generalizations are difficult to make. Taking into account the contribution from atmospheric nitrogen, EPA has developed estimates of NO<sub>x</sub> emissions for most fuel uses [USEPA 1978 & undated]. The EPA emissions coefficients for coal burned in electric utilities and other industrial boilers, respectively, are about 11.5 kg/ton and 9.5 kg/ton. Natural gas and residual oil combustion emissions by electric utilities are slightly lower than emissions from coal (10.95 and 7.29 kg/ton, respectively). Industrial boilers emit a little less NO<sub>x</sub> than utility boilers, on the average, because they are smaller and operate at lower temperatures. Railroad uses of coal can be assumed to be very similar to industrial boilers. Fuel wood is used primarily in residences, or by the paper/pulp industry. High water content tends to keep

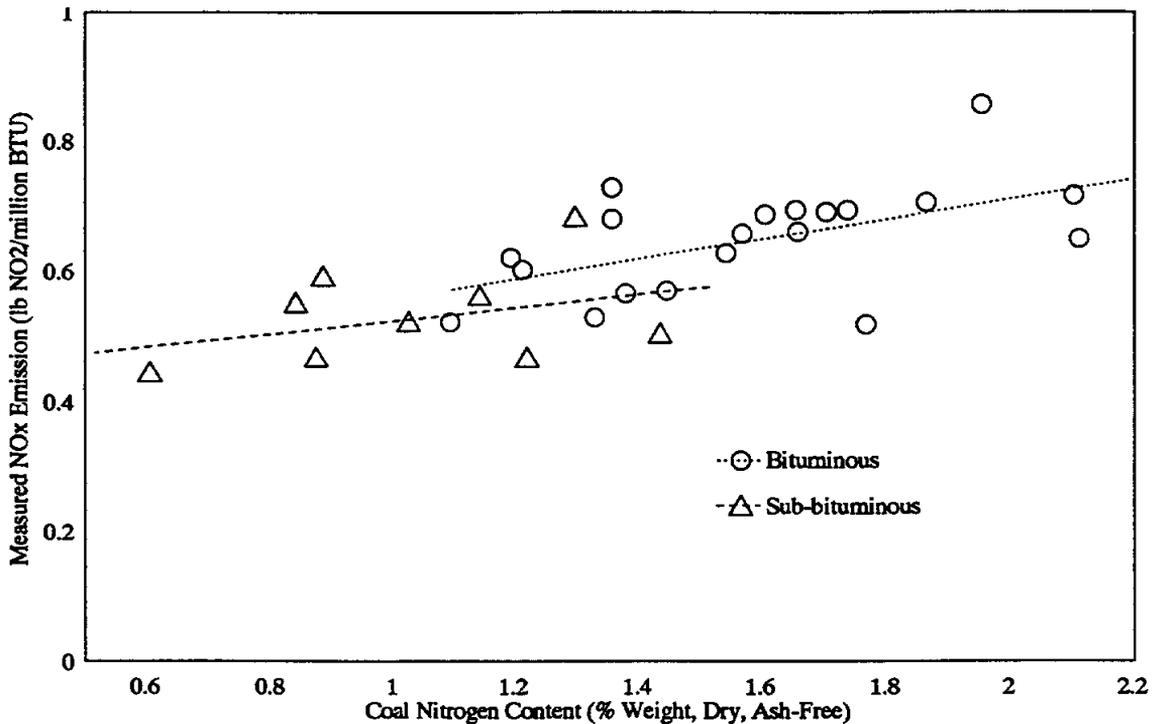


Figure 9: Nitric Oxide Emission as Measured vs. Coal Nitrogen Content  
 Source: [USEPA 1979-f]

temperatures low and minimizes NO<sub>x</sub>.

Historically, the only important technological change affecting NO<sub>x</sub> emissions (apart from automobile emissions controls) has been the increased size and efficiency of utility boilers, especially since the first uses of pulverized coal in the 1920s. It may be noted that, as of 1979, over 99% of U.S. coal-burning utility boilers used either pulverized coal (88%) or cyclones (11%). On the other hand, 60% of industrial boilers use pulverized coal while 40% use stokers. Only 14% of boilers in the commercial residential category (large buildings) use pulverized coal, while the rest use stokers or manual feeds. Western Europe probably approximates the U.S. pattern. However in Eastern Europe and Asia it is likely that stokers still predominate. Use of pulverized coal roughly doubles (11.5/7.1) the NO<sub>x</sub> emissions relative to the use of lump coal in stokers.

The technology of pulverization of coal was initially developed in the nineteenth century. Attempts were made in the late nineteenth century to burn pulverized coal under industrial boilers but they were unsuccessful until approximately 1910. In the twentieth century, a growing concern over fuel economy stimulated attempts at innovation. Pulverized coal was rapidly adopted in electrical generating and industrial plants after World War 1. Design advances that increased the efficiency of the furnaces by eliminating slag and improving combustion followed, as did improvements in pulverizers. By the early 1920s, pulverized coal was producing a 3 to 5 percent gain in efficiency compared to firing with stokers as well as a savings in coal costs [de Lorenzi 1948 :9-32-43; Rosin 1947 :17]. Based on mostly anecdotal historical evidence, we estimate the historical penetration of pulverized coal as shown in Table II. EPA's national emissions estimates for NO<sub>x</sub> are given in Table III.

Emission coefficients for NO<sub>x</sub> are taken from EPA reports [USEPA 1978 & undated] and summarized in *Table IV*.

**Table II: Penetration of Coal Pulverization**

<i>Year</i>	<i>Utilities</i>	<i>Industrial</i>	<i>Comm/Residential</i>
1920	0%	0%	0%
1950	50%-60%	25%-30%	< 5% (?)
1980	99%	60%	14%

*Source: [Ayres et al 1987; Table 3.2]*

**Table III: EPA Estimates of NO<sub>2</sub> Emissions 1940-1980 (Teragrams/yr)**

<i>Source</i>	<i>1940</i>	<i>1950</i>	<i>1960</i>	<i>1970</i>	<i>1980</i>
Highway Vehicles	1.3	2.1	3.6	6.0	7.2
Aircraft	0.0	0.0	0.0	0.1	0.1
Railroads	0.6	0.9	0.7	0.6	0.8
Vessels	0.1	0.1	0.1	0.1	0.1
Off-Highway	0.2	0.4	0.5	0.8	1.0
Mobile Source Total	2.2	3.5	4.9	7.6	9.2
Electric Power	0.6	1.2	2.3	4.5	6.4
Industrial Boilers	*2.3	*2.9	*3.7	*3.9	*3.1
Commercial/Institutional Heat	0.2	0.3	0.3	0.3	0.3
Residential Heat	0.3	0.3	0.4	0.4	0.4
Stationary Combustion Total	3.4	4.7	6.7	9.1	10.2
Chemicals	0.0	0.0	0.1	0.2	0.2
Petroleum Refining	0.1	0.1	0.2	0.2	0.2
Iron & Steel Mills	0.0	0.1	0.1	0.1	0.1
Pulp Mills	—	—	—	—	—
Mineral Products	0.1	0.1	0.1	0.2	0.2
Industrial Total	0.2	0.3	0.5	0.7	0.7
Incineration	0.0	0.1	0.1	0.1	0
Open Waste Burning	0.1	0.1	0.2	0.3	0.1
Forest Fires	0.7	0.4	0.2	0.2	0.2
Other Burning	0.2	0.2	0.2	0.1	0
Waste & Miscellaneous Total	1.0	0.8	0.7	0.7	0.3
Grand Total	6.8	9.3	12.8	18.1	20.4

\* Very questionable (see text)

Source: [USEPA 1986]

Table IV: 1980 NO<sub>x</sub> Emissions Coefficients, Uncontrolled (kg as NO<sub>2</sub>)

Fuel Type	Fuel 10 <sup>9</sup> J/ton	Stationary			Mobile	
		Electric utilities	Industrial boilers	Resid./ Commer.	Highway	Off Highway
Anthracite coal	26.6	N	8.25	8.25	N	N
Bituminous coal	26.25	11.5 (a)	9.1 (b)	6.0 (c)	N	6.0
Lignite	18.0	7. (a)	5.5 (b)	3.4 (c)	N	N
Wood (12% H <sub>2</sub> O)	15.5	N	0.75	0.75	N	N
Residual oil	48.96	7.29	7.02	7.02	N	N
Heating oil	48.19	2.86	2.86	2.72	N	N
Diesel oil	50.80	N	N	N	41.8	54.3
Gasoline (d)	51.54	N	N	N	15.7 urban 17.8 rural	17.8
Jet fuel (kerosine)	51.38	N	N	N	N	N
Natural gas	53.40	10.95	3.13	2.23	N	N

"N" = Not applicable.

- (a) For 1950 assume 8.85 for coal and 5.30 for lignite;  
For 1920 assume 5.60 for coal and 3.20 for lignite.
  - (b) For 1950 assume 7.10 for coal and 4.15 for lignite;  
For 1920 and earlier assume 5.6 for coal and 3.2 for lignite.
  - (c) For 1950 and earlier assume 5.6 for bituminous coal and 3.2 for lignite.
  - (d) For 1950 assume 19.6 urban (70%) and 22.5 rural (30%), or 20.5 average;  
For 1920 assume a composite coefficient of 10, because of lower compression ratios.
- Source: [Ayres *et al* 1987; Table 3.5]

## References

[Axtell 1993]

[Ayres, Ayres & Tarr 1987] Ayres, Robert U., Leslie W. Ayres & Joel A. Tarr, *An Historical Reconstruction of Major Atmospheric Gaseous Emissions in the U.S., 1880-1980*, Technical Report, Variflex Corporation, Pittsburgh PA, 1987.

[Ayres, Norberg *et al* 1989] Ayres, Robert U., Vicky Norberg-Bohm, Jackie Prince, William M. Stigliani & Janet Yanowitz, *Industrial Metabolism, the Environment, & Application of Materials-Balance Principles for Selected Chemicals*, Research Report (RR-89-11), International Institute for Applied Systems Analysis, Laxenburg, Austria, October 1989.

[Crutzen 1976] Crutzen, Paul J., *The Nitrogen Cycle & Stratospheric Ozone*, Nitrogen Research Review Conference, United States National Academy of Sciences, Fort Collins CO, October 12-13, 1976.

[de Lorenzi 1948] de Lorenzi, Otto, *Combustion Engineering*, Technical Report, Combustion Engineering, Inc., New York, 1948.

[Engdahl 1968] Engdahl, Richard B. "Stationary Combustion Sources", in: Stern(ed), *Air Pollution: Sources of Air Pollution & Their Control*, Chapter 32 :4-54 [Series: Environmental Sciences] III, Academic Press, New York, 1968. 2nd edition.

- [Jackson 1968] Jackson. "Re. NO<sub>x</sub>", in: Stern(ed), *Air Pollution: Sources of Air Pollution & Their Control* [Series: Environmental Sciences] III, Academic Press, New York, 1968. 2nd edition.
- [Lim et al 1981] Lim K.J. et al. "NO<sub>x</sub> Combustion Modification", in: Martin(ed), *Emission Control for Industrial Boilers*, Chapter 3 :222-279, Noyes Publications, Park Ridge NJ, 1981. [Reprinted from "Technology Assessment Report for Industrial Boiler Applications: NO<sub>x</sub> Combustion Mod." for EPA 1979]
- [Lotka 1956] Lotka, Alfred J., *Elements of Mathematical Biology*, Dover Publications, New York, 1956. 2nd Reprint edition. [Original title: Elements of Physical Biology, 1924]
- [Lowenheim & Moran 1975] Lowenheim, F.A. & M.K. Moran. "Nitrogen", in: Faith, Keyes & Clark (eds), *Industrial Chemicals*, :462ff, Wiley Interscience, New York, 1975, 4th edition.
- [MacKinnon 1974] MacKinnon, D.J., "Nitric Oxide Formation at High Temperature", *Journal of the Air Pollution Control Association* 24(3), March 1974.
- [Muehlberg et al 1977] Muehlberg, et al. "Phosphate Rock & Basic Fertilizer Industry", in: *Industrial Process Profiles for Environmental Use*, Chapter 22(EPA-600/2-77 023v), Government Printing Office, Washington DC, Dow Chemical Company & Radian Corporation, February 1977.
- [Rosin 1947] Rosin, P.O. "The History of Pulverized Fuel as Reflected by its Economic & Technical Problems", in: *Conference on Pulverized Fuel* :13-44, The Institute of Fuel, London, 1947.
- [Russell & Vaughan 1976] Russell, Clifford S. & William J. Vaughan, *Steel Production: Processes, Products & Residuals*, Johns Hopkins University Press, Baltimore MD, 1976.
- [Schlesinger & Hartley 1992] Schlesinger, William H. & Anne E. Hartley, "A Global Budget for Atmospheric NH<sub>3</sub>", *Biogeochemistry* 15, 1992 :191-211.
- [Shreve 1956] Shreve, R. Norris, *The Chemical Process Industries*, McGraw-Hill Book Company, New York, 1956.
- [Stigliani 1988] Stigliani, William D., "Changes in Valued "Capacities" of Soils & Sediments as Indicators of Non-Linear & Time-Delayed Environmental Effects" *Environmental Monitoring & Assessment* 10, 1988 :245-307.
- [Thiemens & Trogler 1991] Thiemens, Mark H. & William C. Trogler, "Nylon Production: An Unknown Source of Atmospheric Nitrous Oxide", *Science* 251, 1991 :932-934.
- [Williams et al 1992] Williams, E.J., A. Guenther, & F.C. Fehsenfeld, "An Inventory of Nitric Oxide Emissions from Soils in the United States", *Journal of Geophysical Research* 97(D7), May 20, 1992 :7511-7519.
- [ANL 1980] Gaines, L.L. & S.Y. Shen, *Energy & Materials Flows in the Production of Olefins & Their Derivatives*, (ANL/CNSV-9), Argonne National Laboratory, Argonne, IL, August 1980. [for U.S. Department of Energy, Washington, DC].
- [CEN 1990] Chemical & Engineering News, "Production by the U.S. Chemical Industry", *Chemical & Engineering News*, June 27, 1990.
- [CEN 1992] Chemical & Engineering News, "Production by the U.S. Chemical Industry", *Chemical & Engineering News*, June 29, 1992.

- [HISSTAT 1975] United States Bureau of the Census, *Historical Statistics of the United States, Colonial Times to 1970*, Bicentennial Edition, Part 2, United States Government Printing Office, Washington DC, 1975.
- [IEI 1991] Industrial Economics, Incorporated, *Materials Balance Profiles for 33/50 Chemicals*, Draft Report (EPA Contract 68-W1-0009), Industrial Economics, Incorporated, Cambridge MA, September 1991.
- [MINYB 1989] Bureau of Mines, United States Department of the Interior, *Minerals Yearbook 1989*, United States Government Printing Office, Washington DC, 1991.
- [MINYB 1985] Bureau of Mines, United States Department of the Interior, *Minerals Yearbook 1985*, United States Government Printing Office, Washington DC, 1986.
- [MINYB 1980] Bureau of Mines, United States Department of the Interior, *Minerals Yearbook 1985*, United States Government Printing Office, Washington DC, 1981.
- [MINFP 1985] Bureau of Mines, United States Department of the Interior, *Mineral Facts & Problems, 1985 Edition*, Bureau of Mines Bulletin 675, United States Government Printing Office, Washington DC, 1985.
- [MINFP 1975] Bureau of Mines, United States Department of the Interior, *Mineral Facts & Problems, 1975 Edition*, United States Government Printing Office, Washington DC, 1975.
- [USDA 1992]
- [USEPA 1978] United States Environmental Protection Agency, *Mobil Source Emission Factors*, Technical Report (EPA-400/9-78-005), United States Environmental Protection Agency, Washington DC, September 1978.
- [USEPA 1979-e,f] United States Environmental Protection Agency, *Methods of Controlling NO<sub>x</sub> in Combustion*, Technical Report (EPA 600/7-79-178 e,f,g), United States Environmental Protection Agency, Cincinnati OH, 1979.
- [USEPA 1986] United States Environmental Protection Agency Office of Air Quality Planning & Standards, *National Air Pollution Emission Estimates, 1940-1984*, Technical Report (EPA-450/4-85-014), United States Environmental Protection Agency Office of Air Quality Planning & Standards, Research Triangle Park NC, January 1986
- [USNAS 1978] National Academy of Sciences (NAS/NRC), *Nitrates: An Environmental Assessment*, Washington DC, 1978.
- [USNRC 1992] "Human Causes of Global Change" in: Stern, P.C., O.R. Young & D.Druckman (eds), *Global Environmental Change; Understanding the Human Dimension*, Chapter 3, :44-55, National Academy Press, Washington DC, 1992.