

*"Materials-Cycle Optimisation in the
Production of Major Finished Materials"*
CHAPTER 8: NITROGEN-BASED CHEMICALS

by

R.U. AYRES*
and
L. W. AYRES**
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* Professor of Environmental Economics, Sandoz Chair in Management and the Environment, at INSEAD, Boulevard de Constance, Fontainebleau 77305 Cedex, France.

** Research Associate at INSEAD, Boulevard de Constance, Fontainebleau 77305 Cedex, France.

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This chapter is part of a report made for the EC DGXII on a project entitled "**Materials-Cycle Optimisation in the Production of Major Finished Materials**". This project aims at facilitating the identification of longer-term R&D needs for materials-cycle optimisation, especially by using wastes, co-products, or by-products from one process as inputs to other processes. Book publication is envisaged. Following is the list of chapters:

- Chapter 1: Summary and Overview (*Insead ref N°: 95/05/EPS*)
- Chapter 2: Alumina, Aluminium and Gallium (*Insead ref N°: 95/06/EPS*)
- Chapter 3: Copper, Cobalt, Silver & Arsenic (*Insead ref N°: 95/07/EPS*)
- Chapter 4: Chromium Sources, Uses and Losses (*Insead ref N°: 95/08/EPS*)
- Chapter 5: Zinc and Cadmium (*Insead ref N°: 95/09/EPS*)
- Chapter 6: Sulfur and Sulfuric Acid (*Insead ref N°: 95/10/EPS*)
- Chapter 7: Phosphorus, Fluorine and Gypsum (*Insead ref N°: 95/11/EPS*)
- Chapter 8: Nitrogen-based Chemicals (*Insead ref N°: 95/12/EPS*)
- Chapter 9: The Chlor-Alkali Sector (*Insead ref N°: 95/13/EPS*)
- Chapter 10: Electronic Grade Silicon (EGS) for Semiconductors (*Insead ref N°: 95/14/EPS*)
- Chapter 11: Packaging Wastes (*Insead ref N°: 95/15/EPS*)
- Chapter 12: Scrap Tires (*Insead ref N°: 95/16/EPS*)
- Chapter 13: Coal Ash: Sources and Possible Uses (*Insead ref N° 95/17/EPS*)

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CHAPTER 8. NITROGEN-BASED CHEMICALS¹

8.1. Summary

Inorganic Nitrogen (N_2) is a colorless, odorless, tasteless gas that constitutes almost 80% of the atmosphere. In this form it is chemically rather inert and inaccessible to living organisms, as well as to 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.

Nitrogen occurs in all valence states from -3 to +5. The most reduced (-3) form of nitrogen, ammonia (NH_3), is a strong 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 N_2O_5 , which reacts with the water molecule to form nitric acid HNO_3 . Nitric acid deposition is one of the two chief causes of soil acidification and problems like *Waldsterben*. Nitric acid reacts with alkaline salts to form nitrates. Either ammonium salts or nitrates (most are soluble) can be taken up by plants. Thus, nitric acid deposition is also a kind of fertilization (eutrophication) of the environment.

Unfortunately, both types of bio-available nitrogen compounds (i.e. ammonium salts or nitrates) are rather easily lost from soils, either by runoff and erosion, or by bacterial conversion to unavailable forms such as molecular nitrogen (the latter process is known as denitrification). It is the denitrification process that created the nitrogen atmosphere in the first place. Thus the balance between denitrification and nitrogen fixation is one way of characterizing the "nitrogen cycle".

Thus, the limiting factor for life, in most environments — both terrestrial and marine — is bio-available nitrogen. Most biomes are N-limited, despite the evolutionary "invention" of nitrogen-fixing bacteria and their symbiotic relationships with certain plants known as legumes. However, few legumes produce food directly consumable by humans (soya beans being the main exception). This is why nitrogen fertilizers are effective. It is also why N-fertilizers are essential to support agricultural production at the levels needed to support the current human population, and why still further increases will be needed to support expected population increases.

The natural tendency toward thermodynamic equilibrium, in an oxidizing environment, is for reduced nitrogen in the -3 valence state (NH_3) to be oxidized gradually to the +5 valence state (nitrate ion, NO_3^-). In short, without living organisms to cycle the nitrogen between the reduced state (ammonia) and the neutral unoxidized molecular (di-nitrogen) state, all the oxygen in the atmosphere would eventually combine with the nitrogen to form nitric acid. The

eventual result would be an acid ocean, leaving an atmosphere with no free oxygen left in it. No life on such an earth we would be possible.

Life on the earth actually depends on the continuing stability of the nitrogen cycle. This cycle evolved over billions of years to a (nearly) balanced and quasi-stable state. However, as will be seen, the N-cycle is now being rapidly unbalanced — and possibly destabilized — as a result of large-scale industrial fixation of nitrogen, both as NH_3 and as NO_x . The use of nitrogenous fertilizers to enhance the fertility of agricultural soils is probably unavoidable, in view of growing populations and rising standards of living. This being so, it is of utmost importance to minimize unnecessary losses of nitrogen in biologically available form, including wasteful uses of fertilizer itself, losses in chemical processing, dissipative uses of N-based chemicals (such as pesticides, explosives, etc.) and inadvertent NO_x production. While few of these emissions are extremely hazardous as such, their cumulative total may constitute a major threat to the environment.

To minimize unnecessary nitrogen emissions will be a difficult task, since they are so various. A detailed analysis of policy approaches to bring this about is beyond our scope. However, a few comments are relevant. Certainly, a very high priority should go to the development of genetically engineered crop plants capable of N-fixation. Second priority should go to improved means of delivery of N-fertilizer directly to crop plants. Strictly enforced worldwide controls over NO_x emissions from electric power plants and internal combustion engines is another necessary starting point. Since virtually all nitrogen-based chemicals are derived from ammonia, a resource tax (or emissions fee) on ammonia production would tend to reduce wasteful consumption. A targeted tax on other nitrogen-based chemicals, such as explosives, materials of all kinds (virtually all of which are dependent on nitrogen) would have a number of beneficial effects.

Goals for Public Policy: Highest priority to develop plant species capable of N-fixation; strict minimization of NH_3 , N_2O and NO_x emissions from all sources.

8.2. Sources of Fixed Nitrogen

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 (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-content². Of this, Chilean saltpeter was the largest, accounting for 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 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 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. The fourth largest was the Haber-Bosch process (below). Fifth and last, by 1920 the original Birkeland-Eyde process was already obsolete, because of its dependence on very cheap electricity, and then accounted for only 1.5% of synthetic nitrogen.³

The so-called Haber-Bosch process, was first developed by the German firm BASF and commercialized in 1913. 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 70% pure. It is fairly easy to purify the nitrogen further by letting the oxygen react with some other substance, leaving an oxide (H_2O 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 most of the world 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 CO_2 while the hydrogen and nitrogen combine in the presence of a catalyst to form ammonia (NH_3). See *Figure 8.1*. (The subsequent processes to obtain key derivatives are shown in *Figure 8.2*). There 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_2 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.

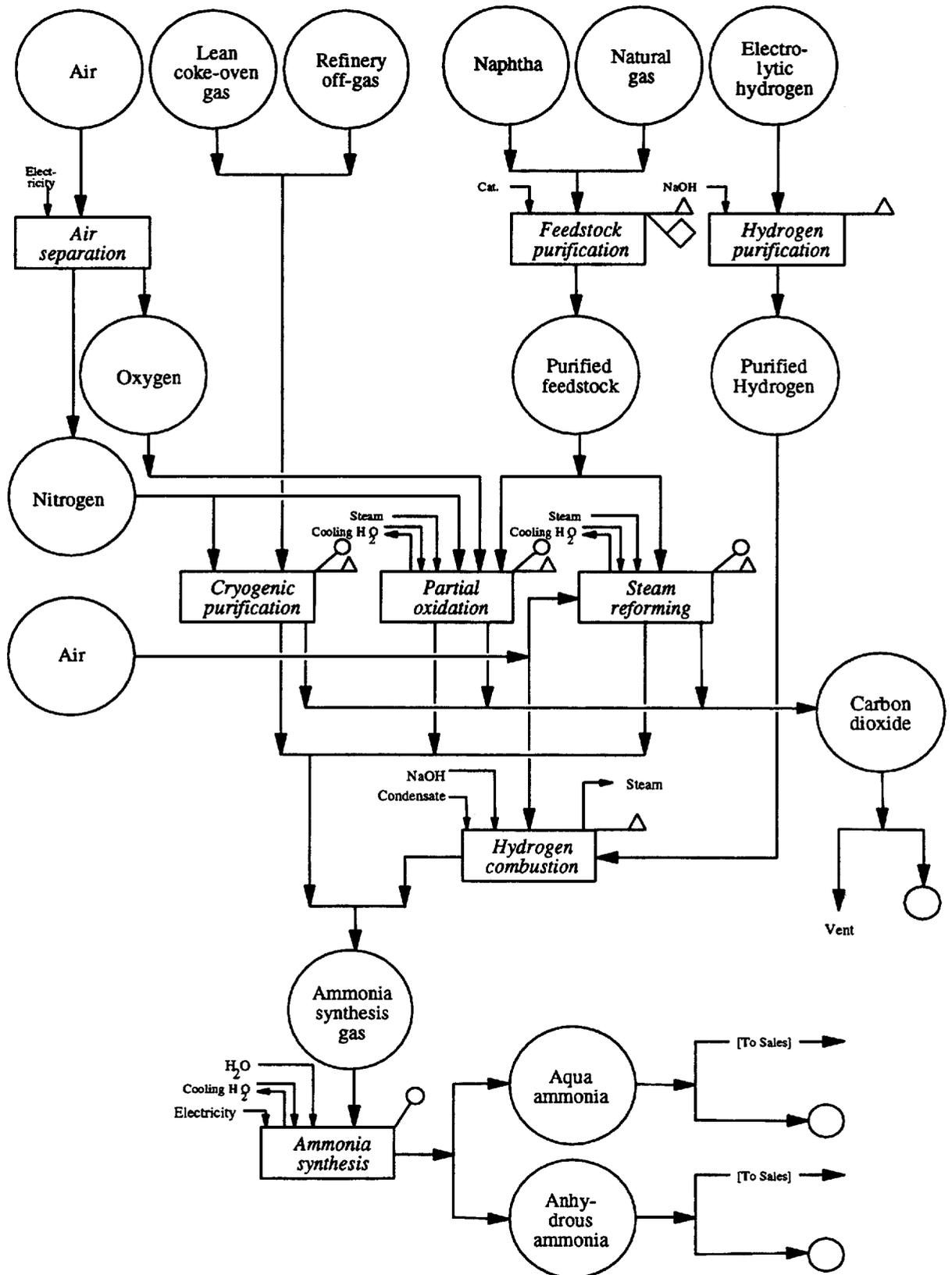


Figure 8.1. Materials-process relationships for ammonia synthesis
 Source: [Muelberg et al 1977; p.30]

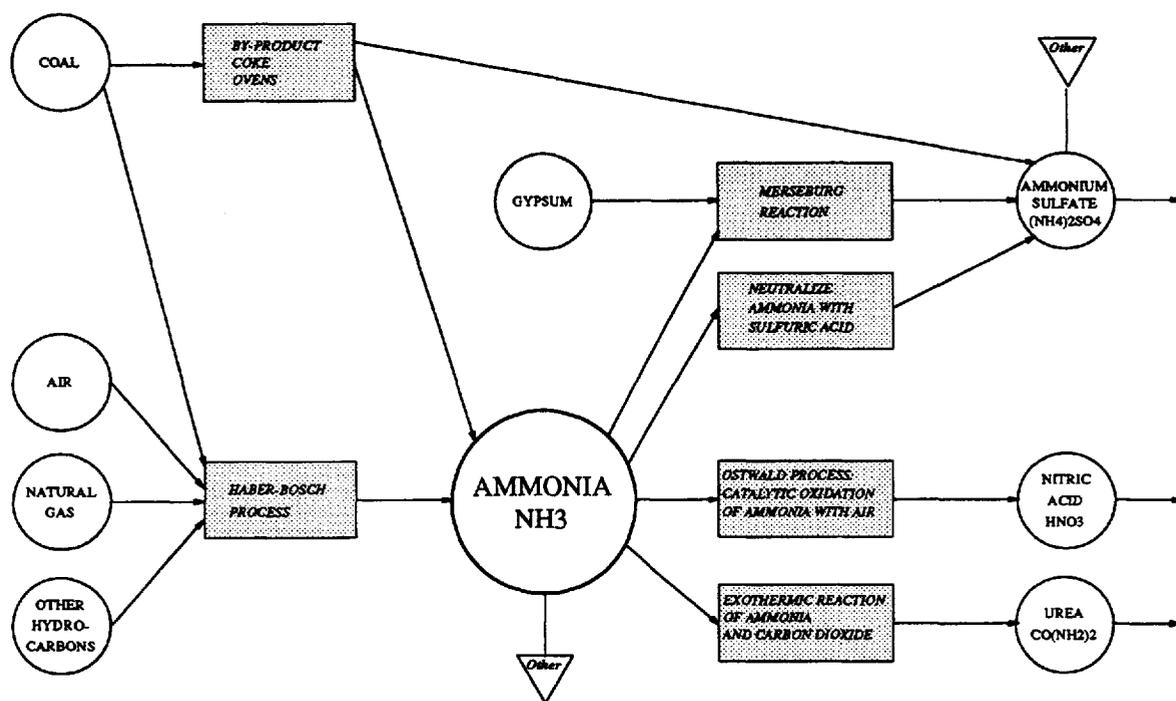


Figure 8.2. Production of ammonia & some key derivatives

Table 8.1. Ammonia (MMT)

Country	Production			Consumption		Home Deliveries		Exports	
	1988	1990	1992	1988	1990	1990	1992	1990	1992
Austria	408.0	410.0	410.0	411.0	413.0	406.2	393.4	3.8	16.6
Belgium/Lux.	365.1 ^a	264.7	500.0	868.0 ^a	85.0 ^a	264.0	500.0		
Denmark				261.7	294.0				
Finland	41.9	23.3	10.0	311.3	324.0	23.3	10.0		
France	1831.7	1588.0	1407.0	1980.0	2032.0	1571.7	1353.8	14.1	53.2
Germany	1824.4	1671.4	2135.8	1649.3	1475.7	1332.4	1917.8	301.7	218.0
Greece	263.4	258.8	139.5	408.5	385.6	257.3	139.5		
Ireland	413.5	395.4	384.3	350.0	308.0	310.7	380.0	84.7	
Italy	1436.5	1197.0	1097.9	1635.0	1254.0	1048.8	1112.2	148.1	7.2
Netherlands	2955.6	3162.5	2666.6	2046.0	2268.0	2262.2	2103.5	955.8	558.7
Norway	411.0	408.2	342.5	494.4	570.0	430.8	342.5		
Portugal	190.1	198.3	100.3	212.4	181.2	177.7	71.0	27.2	9.6
Spain	484.6	469.1	479.2	1082.2	1086.2	479.6	465.3		10.7
Sweden	7.6			180.6	210.1				
Switzerland	31.2	32.0	31.2	47.5	42.0	10.9	31.2		
UK	1137.2	1148.0	760.0	1424.8	1370.0	1018.8	760.0	143.0	108.5
Others (Iceland)	7.6 ^b	32 ^{a,b}		22.6 ^{b,c}	9.2 ^b				
Total W.Europe	11801.8	11258.8	10573.6			9594.4	9580.2	1678.4	982.5
Turkey	282.5	347.5		880.0		868.2			

Source: [Kemira]

Table 8.2. Fertilizers: Western Europe 1990/1991 (MMT)

CONSUMPTION

Country	Anhydrous NH ₃	Am. Sulfur AS	Urea U	Am. Nitrate AN	Calc. AN CAN	Straight N Total	Am. Phosph. APN	NPK	Total comp.	Total N TN
Austria		0.3	2.1		80.5	84.2	3.6	47.9	52.6	136.7
Belgium/Lux.		2.0	1.0		135.0	143.0	2.0	41.0	43.0	186.0
Denmark	62.5	1.3	7.4		132.7	213.2	3.5	157.0	181.7	394.9
Finland			2.4		18.4	20.8		180.4	185.6	206.4
France	33.9	44.2	254.3	1058.8		1942.6		441.8	550.2	2492.8
Germany	17.0	23.0	194.7		1207.6	1530.0		185.0	257.6	1787.6
Greece		39.5	7.4	115.1	54.4	216.4		41.3	211.1	427.5
Ireland		2.0	63.0		134.0	202.0		168.0	168.0	370.0
Italy	1.0	52.0	343.0		203.0	622.0	59.0	133.0	235.0	857.0
Netherlands	2.0	1.0	2.0		315.0	326.0	1.0	65.0	66.0	392.0
Norway			0.6	0.4	16.8	24.6		82.7	86.2	110.8
Portugal		13.9	20.6	1.7	68.1	109.7	4.2	36.3	40.5	150.2
Spain	13.9	98.3	248.0	112.3	234.1	797.7	66.9	193.6	265.8	1063.5
Sweden	0.2	0.1	2.2	10.0	66.4	144.7		52.1	66.8	211.5
Switzerland		2.3	12.5	3.1	32.6	51.0	2.1	10.3	12.4	63.4
UK	4.0		146.0	722.0	50.0	1005.0		520.0	520.0	1525.0
Others (Iceland)				1.3	0.9	2.2		9.1	10.3	12.5
Total W. Europe	134.5	279.9	1307.2	2024.7	2749.5	7435.1	142.3	2364.5	2952.8	10387.8

PRODUCTION

Austria					150	150		64	68	218
Belgium/Lux.		192	18		348	558	4	198	212	770
Denmark					51.2	57.4		119	127.5	184.9
Finland					17.6	17.6		240.7	250.4	268.0
France	34.0	4.0	104.0	650.0		984.0		431.0	497.0	1481.0
Germany	17.0	188.0	90.0		625.0	1080.0		75.0	85.0	1165.0
Greece				115.8	70.8	186.6		58.2	232.8	419.4
Ireland			135.0		144.0	279.0				279.0
Italy	1.0	64.0	266.0		256.0	603.0		153.0	188.0	791.0
Netherlands	2.0	109.0	448.0		966.0	1693.0	21.0	214.0	235.0	1928.0
Norway				0.3		127.6		359.0	389.8	517.4
Portugal		8.9	18.3	5.4	89.0	126.7		31.6	31.6	158.3
Spain	9.1	92.6	224.4	135.2	253.9	773.6	44.7	143.1	187.8	961.4
Sweden		1.2			104.7	111.1		41.9	64.9	176.0
Switzerland					24.6	24.6		2.1	2.1	26.7
UK	4.0	10.0		650.0		680.0			300.0	980.0
Others (Iceland)				1.1	0.5	1.6		8.3	8.5	10.1

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.

Nearly all forms of "fixed" nitrogen are currently derived from synthetic ammonia (*Table 8.1*). Fixed nitrogen (in the form of ammonia and its derivatives) is an interesting case, since the nitrogen is obtained from the atmosphere, combined with hydrogen from natural gas. Most fixed nitrogen is consumed in fertilizer. A detailed account of nitrogen fertilizer production and consumption in Europe is given in *Table 8.2*. In 1991, world production of synthetic ammonia was 94 MMT (N-content).

8.3. Uses of Fixed Nitrogen

Apart from fertilizers, nitro-chemicals are the main basis of most explosives, both industrial and military. Nitrogen-based chemicals are also building blocks for an important class of synthetic fibers, such as nylon. Because a very large number of chemical pathways is involved, and because of secrecy — both industrial and governmental — it is impossible to account fully for nitrogen chemical usage.

8.4. Materials Balance for N-based Chemicals

Apparent U.S. consumption of ammonia in 1988 was 14.746 MMT (N-content), taking into account imports, exports and stock changes [USBuMines 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-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

Table 8.3. Nitric acid production 1989 (MMT)

Austria	.47
Belgium/Lux.	1.35 ^a
Denmark	.36
Finland	.51
France	3.18
Germany	2.31
Greece	.45
Ireland	.28
Italy	1.19
Netherlands	2.40
Norway	1.08
Portugal	.20
Spain	1.25
Sweden	.42
Switzerland	.09
UK	2.80
Total W.Europe	18.33

Source: [Kemira]

in 1988]. In addition, ammonia is used as a household cleaning agent, as an industrial refrigerant, in metallurgy, in pulp production, and in NO_x reduction equipment. These uses constitute a significant fraction of the "unaccounted for" fraction.

The major intermediate between ammonia and "downstream" chemicals is nitric acid. Production of nitric acid in Europe is shown in *Table 8.3*. End uses are indicated in the pie chart, *Figure 8.3*.

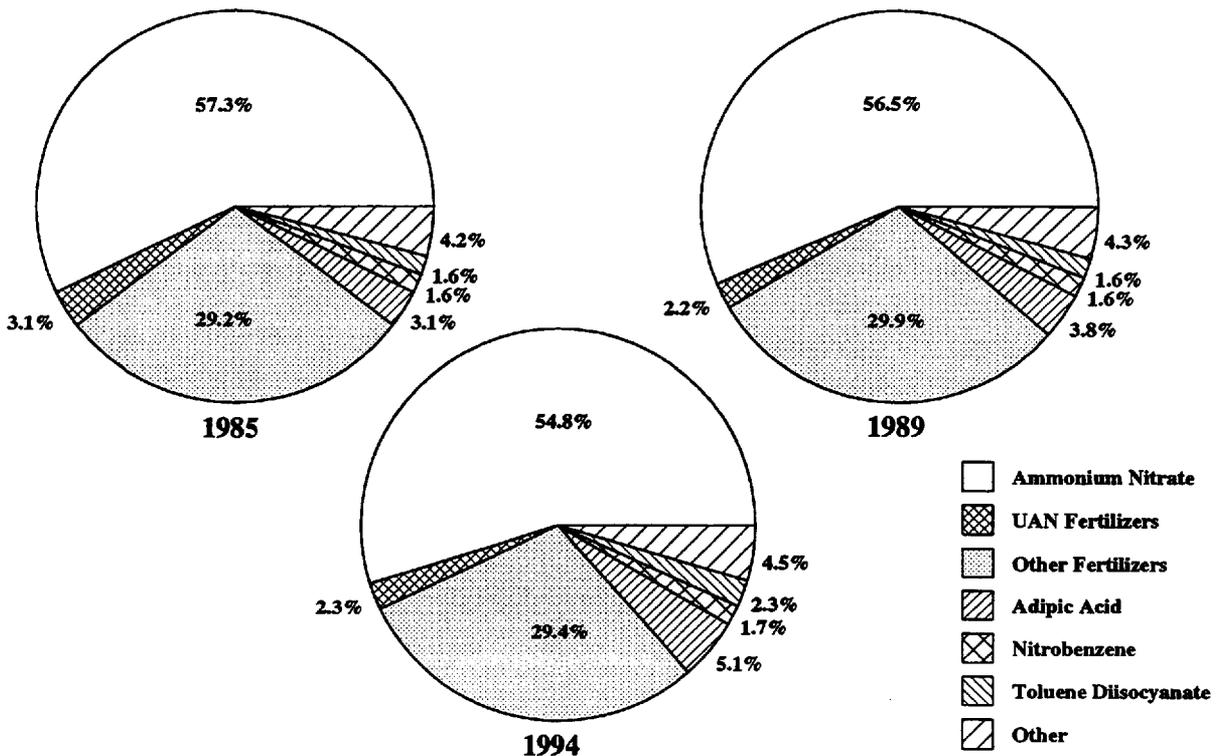


Figure 8.3. Western European consumption of nitric acid. Source: ECOPLAN

Nitric acid production in 1988 in the U.S. 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 as an input. 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 [USBuMines 1989 p.745].

Other industrial uses of nitric acid in the U.S. amounted to 420 KMT(N) according to the Bureau of Mines [USBuMines 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(N) of nitric acid to military use, leaving 105 KMT(N) 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 (HNO_3). Adipic acid production for 1989 was reported as 744 KMT [CEN 1990, cited by Thiemens & Trogler 1991]. This implies total HNO_3 consumption (as N) of 60 KMT. More than half of the nitrogen seems to be converted into nitrous oxide (N_2O) 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.

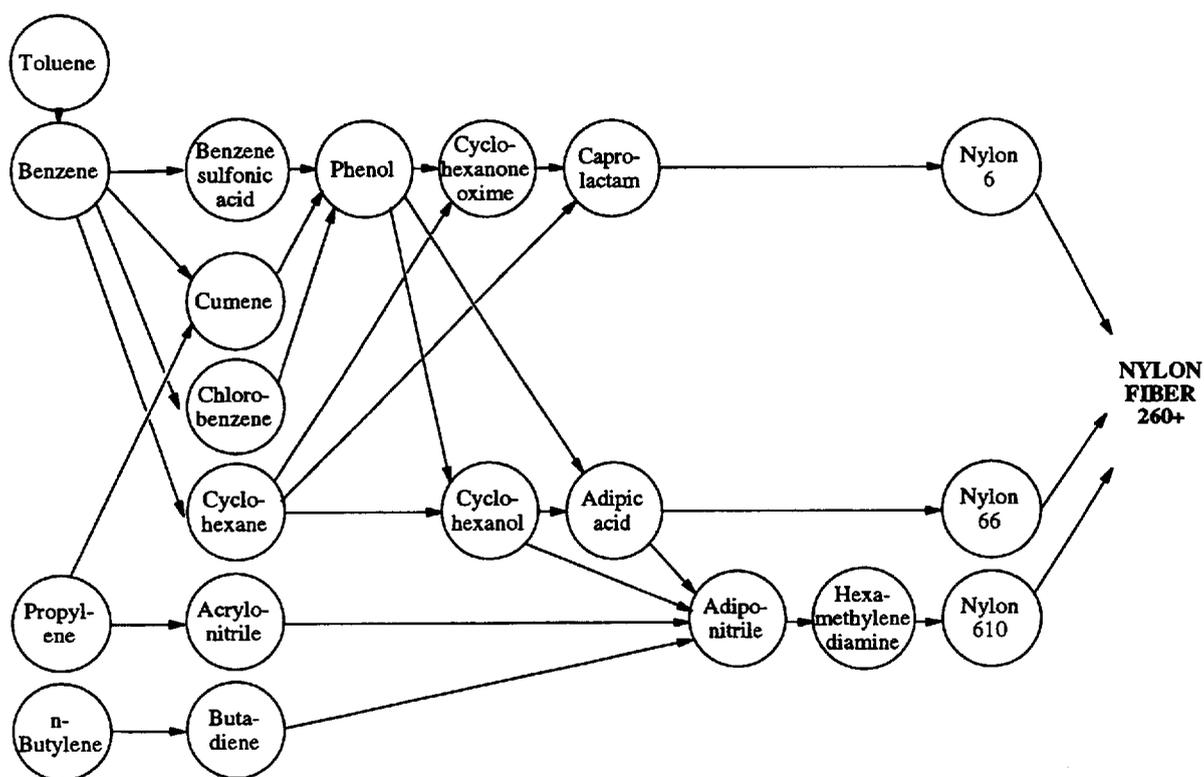


Figure 8.4. Steps in the production of nylon

Total U.S. nylon resin 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 8.4). 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 [Gaines & Shen 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 polyols 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 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.

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, in 1988 [USBuMines 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.

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 [USBuMines 1989 p. 745]. These were for amino-resins, urea-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 (Stamicarbon) 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

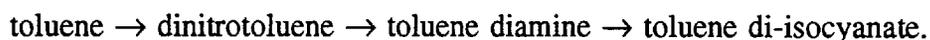
KMT(N), with part of the difference of 68 KMT(N) being recycled as aqueous ammonia (84 KMT(N) consumed as fertilizer [USBuMines 1989 p.746].

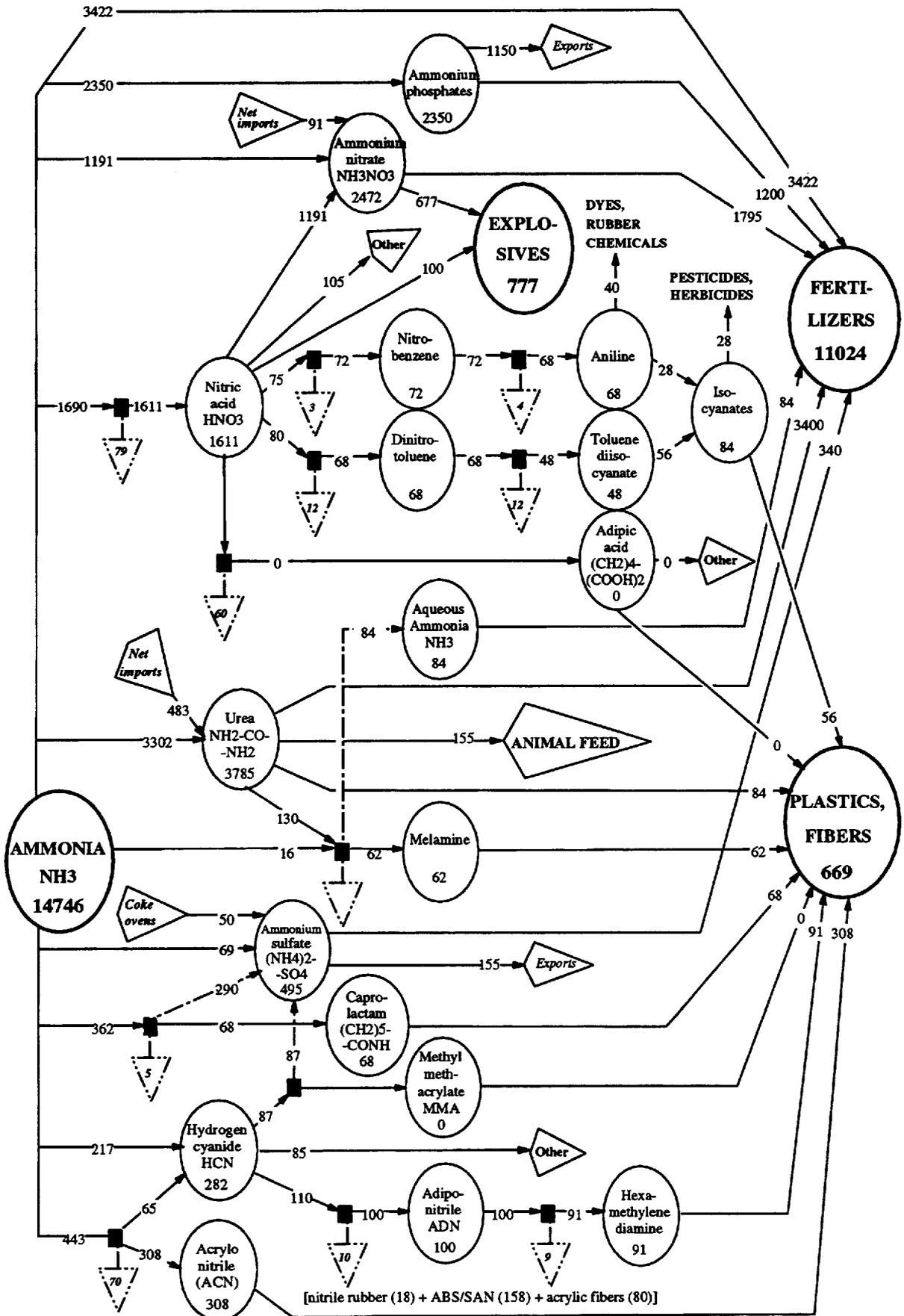
U.S. production of urea-formaldehyde (UF) resin in 1988 was 0.646 MMT. UF resin is a straightforward condensation polymer in which the urea is entirely embodied in the product, which has 26% N-content. On this basis UF resin production accounted for 168 KMT(N). The two resins together embodied 230 KMT(N), 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) [USBuMines 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 for the U.S. in 1988.) The nitrogen content of U.S. caprolactam output in 1988 was 68 KMT(N) [USBuMines 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 of 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) [USBuMines 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 [USBuMines 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.

Toluene di-isocyanate 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 di-isocyanate molecule substitutes two NCO radicals for two of the H atoms on the benzene ring. The conversion sequence is





Data source: author

Figure 8.5. Materials balance of ammonia-based chemical production in the U.S. 1988. (1000 MT N-content)

The overall yield is probably not above 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 di-isocyanate 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.

The N-content of monomers embodied in plastics and resins in 1988 (U.S.) added up to 0.669 MMT. Nitrate and nitro-explosives (excluding amines) accounted for about 0.777 MMT(N). Dyes (aniline, etc) account for at least 0.007 MMT(N). Other uses of nitric acid in the U.S. — including small amounts used in phosphate rock processing and steel pickling — accounted for 0.135 MMT(N). Part of the missing 11% of ammonia goes into other "final" chemicals, including military explosives, pesticides, plasticizers, rubber chemicals and so on. Over 4 MMT of miscellaneous nitrogenous compounds were produced in the U.S. in 1988, including a little less than 1 MMT in the form of alkyl and other amines. We cannot estimate the nitrogen content very accurately, except to say that it is likely to be in the range 10%-20% (higher for explosives). Thus somewhere between 0.4 MMT and 0.8 MMT might consist of nitrogen. We tentatively estimate 0.5 MMT, or approximately one third of the missing 1.6 MMT of nitrogen.

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 8.5*. 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).

8.5. Losses of Fixed (Odd) Nitrogen

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:

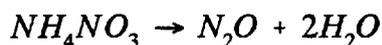
HNO ₃ production (5% loss):	79
Adipic acid production:	30
Acrylonitrile production:	70
Caprolactam:	5
Toluene di-isocyanate:	12
Others:	38
Subtotal of the above:	234

This subtotal identifies probable 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. If this is so, to a reasonably good approximation, we have accounted for 95% of the synthetic fixed nitrogen produced and consumed in the U.S. in 1988.

The 5% remainder unaccounted for would probably be ammonia used for non-chemical purposes, such as household cleaning agents, as noted above. However, there is some possibility of under-counting of the use of nitrogen in mixed fertilizers, where published data seems to be spotty. Lacking further information, we assume the remaining nitrogen is allocated mostly to household cleaning agents and other consumer products.

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 N₂O, one of the more potent "greenhouse" gases. It has been suggested that the N₂O 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 N₂O from adipic acid manufacturing (even assuming 100% conversion of 60 KMT N to N₂O) 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_2O . A straightforward estimate of the reaction products of ammonium nitrate decomposition using ASPEN-PLUS software, suggests that as much as 9% of the N-content could be converted to N_2O [Axtell 1993]. Assuming 777 KMT (N-content) of nitrate explosives produced in the U.S., mainly ammonium nitrate, this suggests that 110 KMT of N_2O might be generated by explosives.

In terms of pollution of the environment, the 3% loss rate suggested above would be insignificant in comparison with dissipative uses of nitrogenous chemicals. Apart from fertilizers and animal feeds, these include industrial explosives, pesticides and herbicides, dyes, surfactants, flotation agents, rubber accelerators, plasticizers, gas conditioning agents, and so on. In fact, except for the plastics and resins (and plasticizers), it is safe to assume that virtually all nitrogenous chemicals are dissipated in normal use, but mainly by other sectors, or final consumers. Over a slightly longer time span — 5 to 10 years — the same is also true of plastics, synthetic rubber, fibers and military explosives.

The ultimate forms of nitrogenous wastes, and even the environmental media into which they are dispersed, are not particularly well-known. One soluble waste generated by many processes is ammonium bisulfate $(NH_4)HSO_4$. This can be converted to ammonium sulfate, in principle, but the conversion is not economic in most cases. Many processes probably dissipate some N as ammonia, some as cyanides (e.g. gold mining) and some as NO_x . The latter contributes to environmental acidification. Adipic acid production, and possibly nitrogenous explosives, seem to produce emissions of N_2O .

8.6. 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_2 or, in some cases, N_2O . 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_2 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^- is 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 $Fe(CN)_2$, ferric cyanide $Fe(CN)_3$, 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"⁴.

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 NO₂, 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. The presence of these in the environment, in conjunction with NO_x seems to be conducive to the formation of nitrosamines.

8.7. Agricultural Emissions 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 (NH₄) ions, nitrate (NO₃⁻) 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 (HNO₃) 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 (NH₃), 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 NAS 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 N_2 or N_2O 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 N_2 (5.6 units) or N_2O (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).

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 [NRC 1992].

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 (10%); for other fertilizers — including anhydrous NH_3 injected directly into the soil — it is about 0.03 [Schlesinger & Hartley 1992, Table 6].

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.

Following this line of reasoning, but without going into all the details, one is forced to conclude that — in a balanced system that is not deficient in nitrogen — crop removals can 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 from the US Department of Agriculture 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 unbalanced case is applicable to many parts of the world where nitrogen has been "mined" from the soil, but the balanced case is more applicable to the U.S. and Europe today.

Animal wastes are a major ammonia pollution problem, especially in the vicinity of animal feed lots and large scale poultry producers. Per capita annual 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 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. Such mass feeding stations are uncommon in Europe, except in the Netherlands. The bulk of this NH_3 was volatilized directly into the atmosphere, although some gets into ground water.

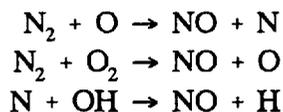
Due to the rapid increase in nitrogen fertilizer use, runoff from agricultural areas is now the dominant source of aggregate nitrogen emissions to the water (and has been since the 1960's). In addition, large-scale animal feed lots have become major point sources of nitrogen emissions (both to water and air) by way of manure and urine⁵. In the extreme case of a heavily urbanized region, however, most N-emissions can evidently be attributed to food processing and consumption wastes (sewage).

As noted above, more than half of the nitrogen in fertilizer added to agricultural soils (in countries where there is a reasonable balance between annual inputs and losses) is taken up by crops and removed by harvesting. Nevertheless, 30% or 40% of that nitrogen is lost unnecessarily to runoff or volatilization. That loss is not only wasteful of a costly (and energy intensive) resource, but it contributes significantly to the growing disequilibrium of the nitrogen cycle. Opportunities to deliver fertilizer more efficiently do exist. One recent study in the Netherlands has estimated that fertilizer application could be reduced by 44% (minimum 28%, maximum 51%) by the adoption of more rational techniques [Worrell *et al* 1994]. This is an area of research that could pay important dividends, both in terms of immediate energy savings and in terms of long term sustainability.

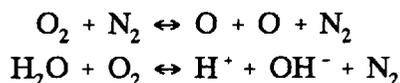
8.8. Emissions of Oxides of Nitrogen (N₂O, NO_x)

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 N₂O, NO and NO₂. In the absence of fuel-bound nitrogen, typically 95—98% of the NO_x in combustion exhaust gas consists of NO. Incompletely oxidized nitrogen is oxidized further to NO₂ in the atmosphere. NO₂ 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, NO₂ reacts with hydrocarbons and oxygen (especially in the presence of UV radiation) to form peroxy-acyl-nitrates (PAN), one of the most irritating and carcinogenic ingredients of urban smog.

The reaction chemistry for NO_x formation by fossil fuel combustion is not completely known, but the most probable sequence for thermal NO_x seems to be the following [Lim *et al* 1981].



where oxygen and hydrogen concentrations are in equilibrium.



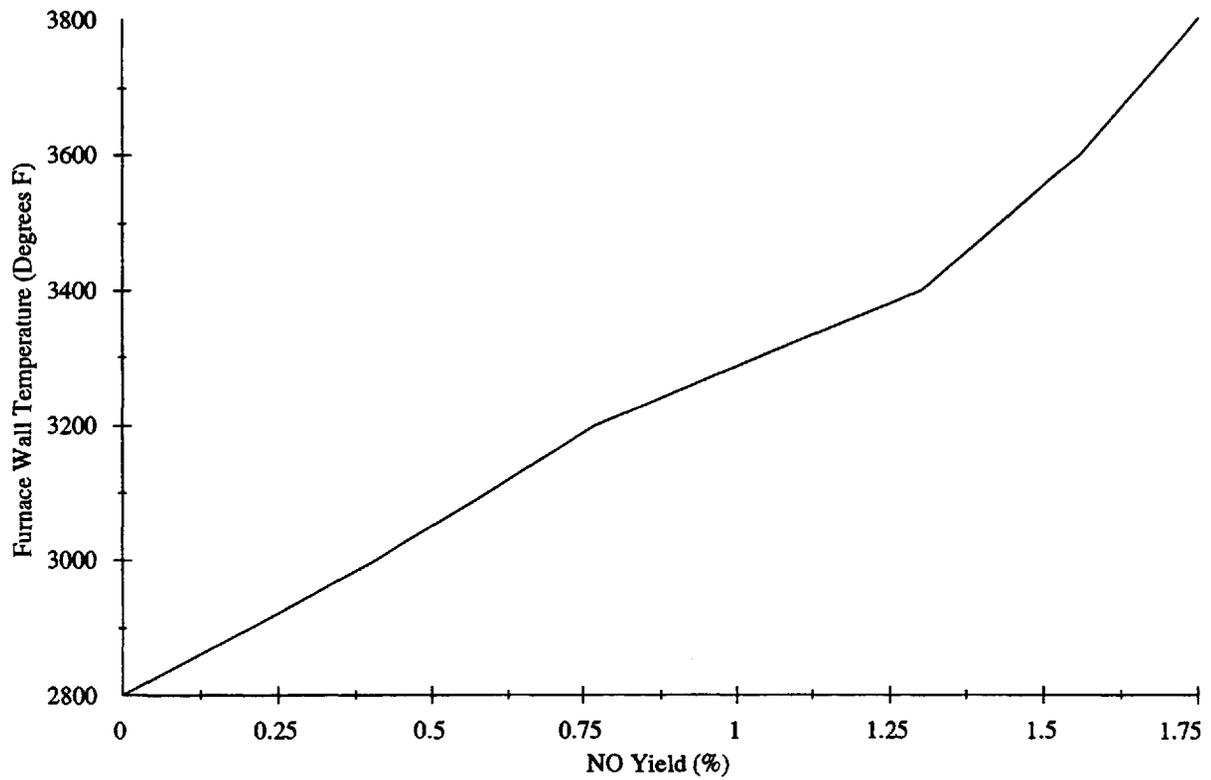


Figure 8.6. NO_x formation vs. temperature, based on measurements at furnace wall. Source; [Ermenc 1956; cited in Engdahl 1968]

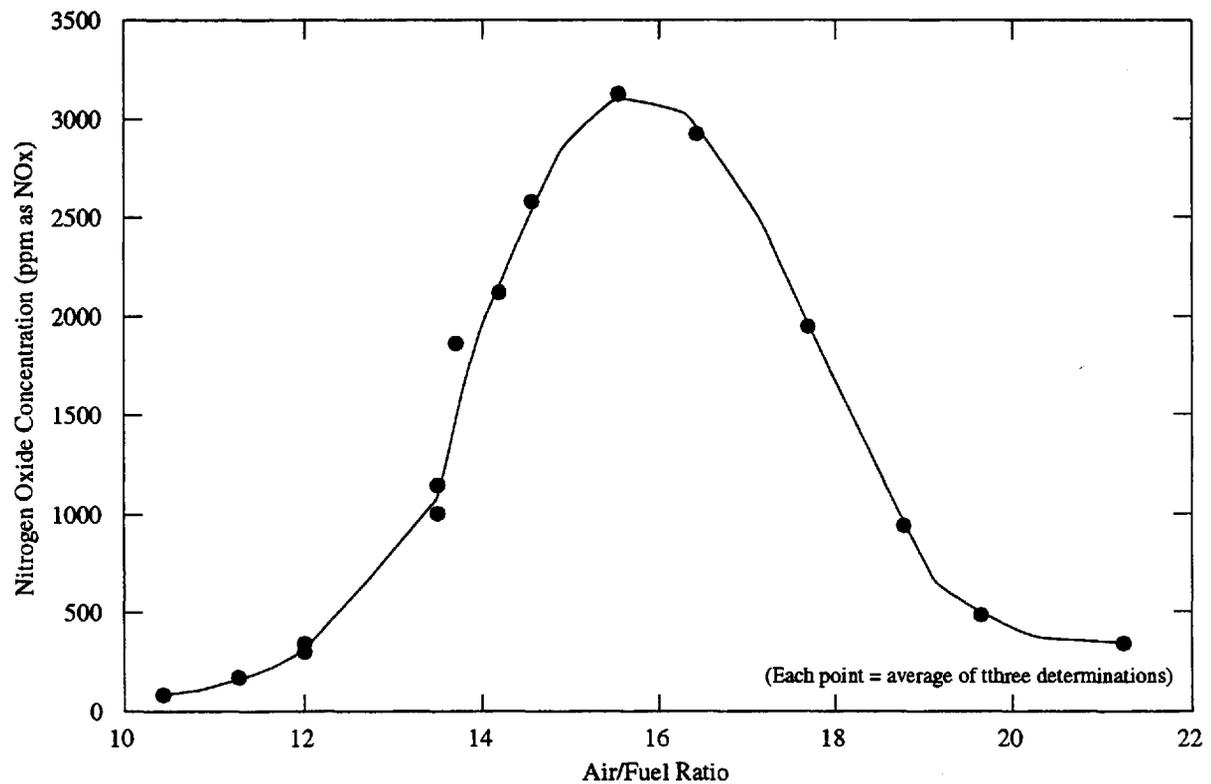


Figure 8.7. Influence of air-fuel ratio on concentration of NO_x in exhaust gas. Source: [adapted from Jackson 1968, Figure 5a]

The reaction rate for 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 NO levels in heated mixtures of N_2 and O_2 at atmospheric pressure is an increasing function of temperature (*Figure 8.6*).

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_x 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_2 concentration times the square root of O_2 concentration, times residence time in the flame. Because of these relationships, air/fuel ratio is a dominant factor in determining NO_x emissions in the absence of fuel-bound nitrogen. *Figure 8.7* shows typical NO_x (NO , NO_2) emissions as a function of air/fuel ratio for automobile gasoline engines [Jackson 1968].

For smoldering fires, or "rich" fuel air mixtures, NO_x production is negligible. However for "lean" fuel air mixtures, it becomes increasingly significant. Thus, NO_x 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 biomass⁶. Thus, fuel-bound nitrogen in all organic materials, as well as in fossil fuels (in coal and residual oil) also contributes to both N_2O and NO_x emissions. Apparently N_2O — one of the most potent "greenhouse gases" — is associated *only* with fuel-bound nitrogen.

Median nitrogen content of US coals corresponds to approximately 1350 Ng/J of NO_2 , assuming 100% conversion; the 25—75 percentile range is fairly narrow, viz. 1250—1400 Ng/J [Lim *et al* 1981]. *Figure 8.8* shows measured relationships between coal nitrogen content in percent by weight and *measured* NO_x emissions. The median NO_x (as NO_2) emission level is about 270 Ng/J. The 25—75 percentile range for bituminous coal combustion corresponds to NO_x (as NO_2) 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_x , the average conversion fraction for fuel-bound nitrogen to NO_x would be $270/1350 = 0.2$.

The relative contribution of fuel-bound nitrogen to NO_x emissions from combustion is not yet completely understood. However studies have shown that the contribution of fuel bound N to total NO_x 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_x , depending on conditions of combustion. No data for 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_x 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 10.4 kg/tonne and 8.6 kg/tonne. Natural gas and residual oil combustion emissions by electric utilities are slightly lower than emissions from coal (9.95 and 6.6 kg/tonne, respectively). Industrial boilers emit a little less NO_x than utility boilers, on the average, because they are smaller and operate at lower

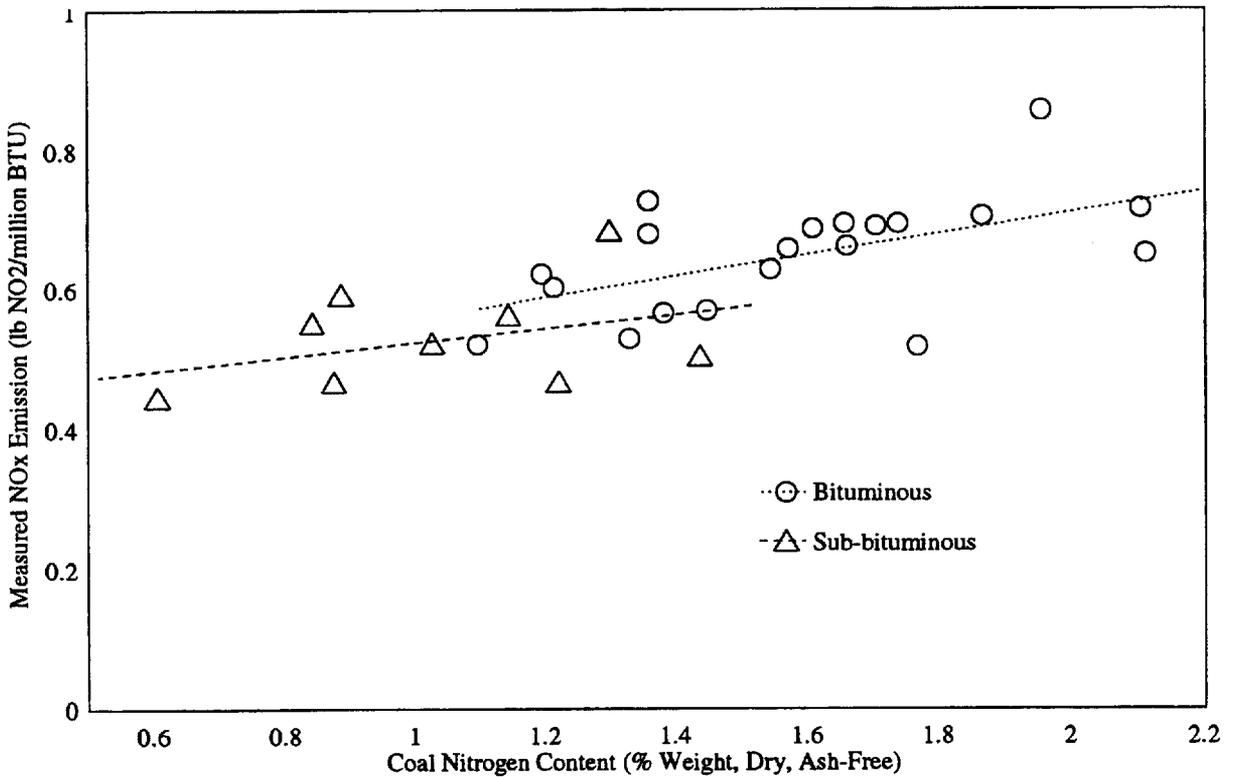


Figure 8.8. Nitric oxide emission as measured vs. coal nitrogen content. Source: [USEPA 1979-f]

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 temperatures low and minimizes NO_x .

8.9. Environmental Impacts of Fixed (Odd) Nitrogen

There are three long term impacts of importance. First, N_2O is a greenhouse gas, contributing up to 10% of the total impact. Second, NO_x contributes about one third of the environmental acidification impact (the other two thirds being due to SO_x). Third, large scale emission of NO_x as well as large scale use of synthetic nitrogen fertilizers may be significantly enhancing the amount of biologically available nitrogen on land. (In fact, the multiplier cannot be stated precisely, but it could easily be 200%). Runoff, in turn, causes — or may cause — eutrophication effects in offshore waters.

Long-term consequences of these effects cannot be foreseen accurately, absent a reliable and quantifiable model of the N-cycle and its interaction with the Sulfur-cycle and the Carbon-cycle. Such a model may not be possible, given the complexity and non-linearity of the system.

8.10. Technologies & Policies

The overall task of public policy must be to minimize unnecessary human interference with the natural N-cycle. This means, in effect, to minimize total emissions of synthetic nitrogen-based chemicals into the environment, from any source whatever.

The first, and most obvious, source of N-emissions is the use of synthetic fertilizers. Whereas natural N-fixation processes synthesize only what is necessary and make it directly available to the plant, the industrial analog is rather inefficient and allows much of the nitrogen to go to waste. What this means, in practice, is that the excess fertilizer moves into other environmental media, whether the air, the surface waters or the ground water. The end result of surface runoff is likely to be eutrophication of lakes or streams — especially estuarine zones offshore. Denitrification bacteria can eliminate the excess, but some is emitted to the air as nitrous oxide, N_2O . This can lead to anoxia and fish kills, among other problems. Nitrates and nitrites in ground water are potentially harmful to animals that may eventually drink the water. Nitrogen (as ammonia) volatilized to the air generally ends up by reacting with sulfur oxides, ending as ammonium sulfate, a fertilizer. This is deposited with the rain, over both land and sea, as does the NO_x from fossil fuel combustion (which is deposited as acid, and helps to acidify the soil). Acidification of agricultural land can be countered by spreading limestone, but acidification of forests cannot be reversed, except by very slow natural processes.

The long-term solution must be to stop using synthetic nitrogen fertilizer at all. The technical solution is biological nitrogen fixation. In principle, this should be within the domain of genetic engineering. Unfortunately, up to now very little R&D investment has been directed to this end. One way to change this would be for government to subsidize this type of research directly. Another approach would be to raise the price of synthetic fertilizers enough to induce farmers to return to the use of animal manure and leguminous crops. This would also create a much more attractive market for genetically engineered N-fixing crops.

Other nitrogen-based chemicals should also be banned or discouraged over time. For one thing, explosives are largely based on nitrogenous compounds. To ban some explosives and heavily tax others would have several beneficial effects. It would be a form of indirect arms control, for one thing. It would also increase the costs of mining virgin ores and fuels in comparison to recycling metals and energy conservation. An outright ban on some uses of nitrogen chemicals (such as cyanidation in gold and silver mining) would probably be helpful, for instance.⁷

Obviously radical changes of this magnitude cannot be accomplished quickly. Quite apart from the impact on chemical producers, the disruptive effects on agriculture will be enormous. But if the relative prices of N-chemicals were to rise gradually (*vis a vis* human labor) over a long period of time, the end-result would eventually occur automatically through the agency of the "invisible hand" of the market. This change in relative prices (or costs, depending on one's point-of-view) is the domain of government. It can be accomplished through a combination of regulation and tax policy, especially by reducing direct and indirect taxes on labor and increasing taxes on fuels and natural resources.

References(8)

- [Ayres *et al* 1988] Ayres, Robert U., Leslie W. Ayres *et al*, *An Historical Reconstruction of Major Pollutant Levels in the Hudson-Raritan Basin 1800-1980*, Technical Memorandum (NOS OMA 43), National Oceanic & Atmospheric Administration, Rockville MD, October 1988. [3 Vols]
- [Ayres *et al* 1989] Ayres, Robert U., Vicki 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.
- [Ayres *et al* 1993] Ayres, Robert U., Vicki Norberg-Bohm & Leslie W. Ayres, *Industrial Metabolism of Nitrogen*, Working Paper (93/11/EPS/TM), INSEAD, Fontainebleau, France, October 1, 1993.
- [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 :39ff.
- [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.
- [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.
- [Gaines & Shen 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]
- [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.
- [Jackson 1968] Jackson. "Re. NO_x", 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_x 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_x 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, Frederick A. & Marguerite K. Moran, *Faith, Keyes, & Clark's "Industrial Chemicals"*, Wiley-Interscience, New York, 1975. 4th edition.
- [NAS 1978] National Academy of Sciences (NAS/NRC), *Nitrates: An Environmental Assessment*, Washington DC, 1978.
- [NASNRC 1992] National Academy of Sciences (NAS/NRC). "Human Causes of Global Change", in: *Global Environmental Change; Understanding the Human Dimension*, Chapter 3 :44ff, National Academy Press, Washington DC, 1992.

- [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 NH₃", *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.
- [USBuMines 1989] United States Bureau of Mines, *Minerals Yearbook*, United States Government Printing Office, Washington DC, 1989.
- [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] United States Environmental Protection Agency, *Methods of Controlling Nox in Combustion*, Technical Report (EPA 600/7-79-178 e,f,g), United States Environmental Protection Agency, Cincinnati OH, 1979.
- [USEPA undated] United States Environmental Protection Agency, *Compilation of Air Pollutant Emission Factors*, Technical Report (AP-42), United States Environmental Protection Agency, Research Triangle Park NC, undated. [Supplements 1-13]
- [Worrell *et al* 1994] Worrell, E., B. Meuleman & K. Blok, "Energy Savings by Efficient Application of Fertilizers", unpublished report, Utrecht University, The Netherlands, 1994.

Endnotes(8)

1. This chapter was based in part on earlier work by the authors [Ayres *et al* 1988], and expanded in the course of a 1988 summer study at IIASA [Ayres *et al* 1989]; the latter was updated again in a working paper "Industrial Metabolism of Nitrogen" by the authors together with V. Norberg-Bohm (then at Harvard, now at MIT). The global nitrogen disequilibrium problem was first discussed in a 1992 working paper "Industrial Metabolism and the Grand Nutrient Cycles" by R.U. Ayres, based on a presentation at a summer workshop of the Global Change Institute, Snowmass, Colorado, August 1992. The latter, in turn, led to a collaborative paper "Industrial Metabolism and the Grand Nutrient Cycles" with R. Socolow and W. Schlesinger, in Socolow *et al* (eds) *Industrial Ecology and Global Change*, Cambridge University Press (in press).
2. For a detailed discussion and breakdown see A. J. Lotka [Lotka 1956, Chap. XVIII].
3. 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.
4. The terminology is due to [Stigliani 1988].
5. 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.

6. In coal the range is between 0.6% and 2% by weight (*Figure 8.8*). 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.
7. The objection will be made that to ban cyanidation would invite the use of mercury for extracting gold and silver from low grade ores, as was done in the 19th century. This should not necessarily be banned, however, but rather taxed at a rate high enough to ensure virtually 100% recycling of metallic mercury.