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R&D**NITROGEN CONSUMPTION IN THE UNITED STATES****by****R. U. AYRES*****and****L. A. FEBRE******2000/19/EPS/CMER**

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* The Sandoz Chaired Professor of Management and the Environment, Director of the Centre for the Management of Environmental Resources (CMER) at INSEAD, Boulevard de Constance, 77305 Fontainebleau Cedex, France.

** Research Assistant at the Centre for the Management of Environmental Resources, at INSEAD, Boulevard de Constance, 77305, Fontainebleau Cedex, France.

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Nitrogen Consumption in the United States

L. A. Febre and R. U. Ayres
CMER, INSEAD
Fontainebleau, France
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Executive Summary

Nitrogen is one of the key component elements in biological systems, but it also plays an increasingly important part in other areas of a modern industrial system. The starting point for all N-based chemicals is ammonia. This paper presents 1996 production and use statistics for ammonia and its most important derivatives. It also characterizes the key production processes and environmental emissions. Finally, we summarize losses and emissions of nitrogen within the sector.

Table of Contents

Nitrogen's Role in Biological and Industrial Systems	1
Production and Statistics of Nitrogen Based Chemicals	3
I. Ammonia	3
II. Ammonia's Sub-products	5
1. Ammonium phosphates	5
2. Nitric acid	6
2.1 Ammonium nitrate	9
2.2 Explosives	10
2.3 Nitrobenzene	12
2.4 Aniline-A	13
2.5 Toluene diisocyanate	14
2.6 Dinitrotoluene	14
2.7 Isocyanates	15
2.8 Adipic acid	16
3. Urea	18
3.1 Melamine	19
3.2 Aqueous ammonia	20
4. Ammonium sulfate	20
5. Caprolactam	21
6. Hydrogen cyanide	21
6.1 Methyl methacrylate	23
7. Acrylonitrile	24
7.1 Adiponitrile	25
7.2 Hexamethylenediamine	25
III. Conclusion	26
Appendix I. U.S. Nitrogen Consumption in 1996	28
Appendix II. U.S. Nitrogen Wastes and Emissions in 1996	29
Appendix III. World Nitrogen Consumption in 1996	30
Appendix IV. Comparison of Experimental vs. Simulated Emission Factors For Detonation of Explosives	31
References	32

List of Tables

Table 1	Principal Activities Producing N ₂ O	7
Table 2	Results of the Simulation of NO Production (Stage One of the Oswald Process) Using Aspen Plus TM	8
Table 3	Waste Products of Nitric Acid Production in 1996	8
Table 4	Classification of Explosives Used by the US Bureau of Census	10
Table 5	Statistics of Industrial Explosives and Blasting Agents Sold for Consumption in the United States	10
Table 6	Explosive's Use Emissions	11
Table 7	Main Uses for Aniline	13
Table 8	Main Uses for Toluene Diisocyanate	14
Table 9	NO _x Emissions from Adipic Acid Facilities in the U.S.	17
Table 10	Main Uses for Urea	18
Table 11	Main Uses for Melamine	19
Table 12	Main Uses for Caprolactam	21
Table 13	Main Uses for Hydrogen Cyanide	22
Table 14	Main Uses for Methyl Methacrylate	23
Table 15	Main Uses for Acrylonitrile	24

List of Figures

Figure 1	Fixed Nitrogen Consumption in the United States in 1996	3
Figure 2	Fixed Nitrogen Consumption in the United States in 1996	3
Figure 3	Ammonium Phosphates Consumption in the United States in 1996	5
Figure 4	Nitric Acid Consumption in the United States in 1996	6
Figure 5	Ammonium Nitrate Consumption in the United States in 1996	9
Figure 6	Explosive's Consumption in the United States in 1996	11
Figure 7	Nitrobenzene Consumption in the United States in 1996	12
Figure 8	Isocyanates Consumption in the United States in 1996	16
Figure 9	Urea Consumption in the United States in 1996	19
Figure 10	Ammonium Sulfate and Caprolactam Consumption in the United States in 1996	21
Figure 11	Hydrogen Cyanide and Acrylonitrile Consumption in the United States in 1996	22
Figure 12	U.S. Nitrogen Consumption in 1996	27

Nitrogen's Role in Biological and Industrial Systems

Nitrogen is one of the most important elements on Earth making up almost 80% of the atmosphere. Molecular nitrogen (N_2) is a colorless, odorless, and tasteless gas that is rather inert and inaccessible to living organisms. An illustration of nitrogen's inaccessibility is respiration. In this process, nitrogen cannot be metabolized and it is breathed out. Nonetheless, it is essential to life and it is a vital ingredient of proteins.

Production and consumption of N-chemicals has created ecological problems. One of the main concerns is the atmospheric emission of N_2O and NO_x . Problems such as smog and excessive acid rain can be attributed to nitrogen emissions. NO_x emissions are regulated but not all facilities are following the rules. Implementation of emission abatement treatments as well as stricter monitoring systems should be enforced. However, N_2O represents an even bigger ecological threat given that it is not regulated and its emissions contribute considerably to the greenhouse effect.

Not only production facilities raise serious ecological concerns, but also end uses contribute to the pollution problem. Even when fertilizers themselves are not considered dangerous, their abuse is provoking global changes as well as local health hazards. In farming regions undergoing heavy fertilization, high nitrate levels have been related to certain cancers and to methemoglobinemia, a life-threatening disease affecting infants. Moreover, excess of N-based fertilizers causes water eutrophication of lakes and rivers and also affect soil's pH contributing to its acidity. Excess acidity can lead to nutrients loss in the soil and to release of heavy metals into underground supplies.

Atmospheric nitrogen is composed of a simple diatomic molecule united by a triple bond. This chemical bond is one of the strongest known ($\Delta H_{\text{dissociation}} = 944.7$ KJ/mol) and it's also the main cause of its inertness. In fact, this property has allowed life to evolve in the planet. A more active nitrogen would have created conditions where life would have been impossible like, for example, a nitric acid ocean.

In order for plants and animals to use nitrogen, it has to be broken down into more reactive compounds that are easier to metabolize. Breakage of the nitrogen bond occurs naturally by two mechanisms. One mechanism takes place during thunderstorms, where lightning supplies enough energy to split the N_2 molecule. Nitrogen then reacts with oxygen to form nitrogen oxides; which later dissolve in water, forming nitrous and nitric acids. These are eventually deposited on the ground as acid rain and combine with natural alkaline elements nurturing plants.

The other mechanism for nitrogen fixation occurs constantly in legumes' root. In this process, Rhizobium bacteria, colonizing the roots, directly convert N_2 into useful forms, such as ammonia compounds, ready for plants' absorption. Then, when animals eat plants, their organisms turn nitrogen into proteins. Later, when they die, denitrifying bacteria release N_2 back to the atmosphere. This whole process is known as the nitrogen cycle.

These available nitrogen sources are very limited and are not enough to meet human agricultural and industrial demand. As a consequence, synthetic industrial methods, like the Haber-Bosch process for ammonia, have been developed. It is estimated that at least two billion people today are alive because the proteins in their bodies are built with nitrogen that comes from synthetic ammonia processes [i].

Ammonia is the only useful nitrogen compound that is produced from atmospheric air. Nevertheless, the commercial synthesis of ammonia did not begin with the peaceful use of fertilizers. It was driven by nations desire to be self-sufficient, not only in fertilizers, but also in the production of explosives at the beginning of this century.

In 1920 there were five different sources of biologically available nitrogen. The first and biggest source (30%) was Chilean saltpeter (NaNO_3). The second largest was ammonium sulfate from by-product coking of coal. In fact, about 0.86 kg of NH_3 can be extracted from a ton of bituminous coking coal. However, its output could not be expanded above the limited amounts available from coal usage. The third source (20%) was obtained from calcium cyanamide. This process was still commercially significant in the 1950's, but it was then obsolescent. The fourth largest process was the Haber-Bosch developed by the German firm BASF. Fifth and last, the Birkeland-Eyde process, where nitrogen is oxidized in the atmosphere in the presence of an electric arc. However, by 1920 it was already obsolete.

Nowadays, virtually all of the world's ammonia is produced by the Haber-Bosch process and is ultimately used as fertilizers. Other important applications for this compound are plastics, dyes, and drugs. Some of the principal intermediaries synthesized from ammonia are:

- Nitric acid, used in dyes, rubbers, herbicides, pesticides and plastics
- Urea, used as a fertilizer, animal feed, and in melamine production
- Ammonium phosphates, used as fertilizers
- Ammonium nitrates, used as fertilizer and in explosives' production
- Ammonium sulfate, used in fertilizers and in other industries
- Caprolactam, used in plastics and fibers' production
- Acrylonitrile, used in the production of nylon
- Hydrogen cyanide, used in plastics and fibers.

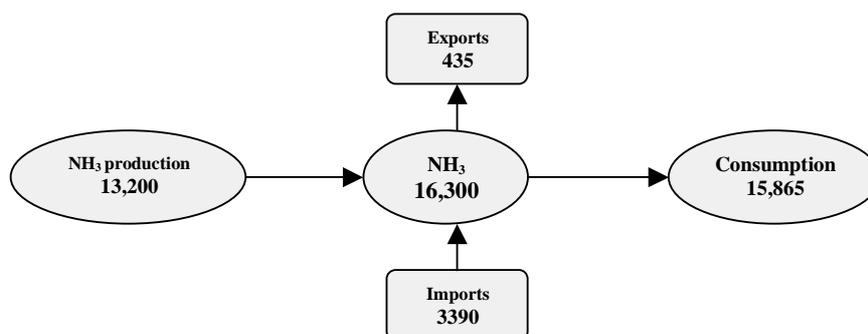
The extensive use of nitrogen-based chemicals is affecting the very subtle equilibrium of the nitrogen cycle. It is therefore important to keep track of all nitrogen-based chemicals produced, their end uses, and production emissions. This way we can have a better idea of the magnitude of the problem we have created.

Production and Statistics of Nitrogen Based Chemicals

I. Ammonia

Ammonia is the most important building block of the world's nitrogen industry and is the starting material for many primary nitrogen products. The United States is the second world's largest consumer and producer of ammonia, following China. In 1996, the U.S. production of anhydrous ammonia was 13,200,000 tonnes of contained nitrogen. Imports for consumption were 3,390,000 tonnes (N) and exports 435,000. Apparent consumption of nitrogen plus wastes was 15,865,000 tonnes (N), as shown in Figure 1, calculated as the production plus imports minus exports. Statistics above do not consider stock held by producers and consumers.

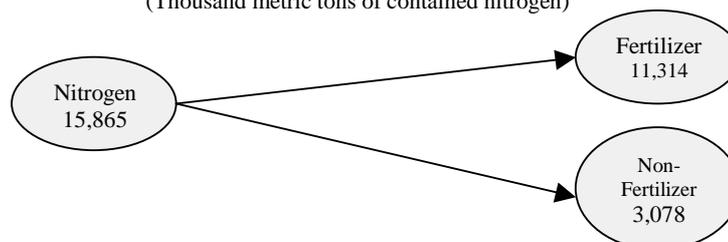
Figure 1. Fixed Nitrogen Consumption in the United States in 1996
(Thousand metric tons of contained nitrogen)



Source: Kramer, U.S. Geological Survey, 1997

Of the total amount of anhydrous ammonia consumed in the U.S. in 1996, 11,314,000 tonnes (N) were used in fertilizers while 3,059,000 tonnes were used in non-fertilizer products (see Figure 2). Principal products synthesized from ammonia are urea, ammonium phosphates, ammonium nitrates, nitric acid, and ammonium sulfates. Other important products include hydrogen cyanide and acrylonitrile.

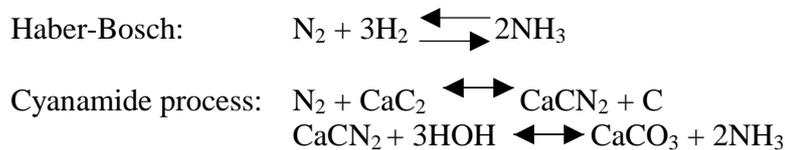
Figure 2. Fixed Nitrogen Consumption in the United States in 1996
(Thousand metric tons of contained nitrogen)



Based on the overall nitrogen material balance:

- 25% of ammonia is used directly as a fertilizer
- 59% is used in manufacturing urea, ammonium nitrate, ammonium phosphate, ammonium sulfate, and nitric acid
- 7% is used in manufacturing acrylonitrile, hydrogen cyanide, and caprolactam
- 9% includes miscellaneous¹, undercounts, and losses.

Industrially, ammonia is made using the Haber-Bosch process, which converts nitrogen gas in the air into ammonia. This is done by combining air with hydrogen at high temperatures and pressures in the presence of a catalyst. It is also obtained as a by-product of the destructive distillation of coal. Furthermore, ammonia can be prepared synthetically by the cyanamide process, where nitrogen gas is combined with calcium carbide (CaC₂) at high temperatures to form calcium cyanamide and carbon. Calcium cyanamide is then reacted with steam to form calcium cyanamide and ammonia [ii]. However, the last cyanamide plant in the Western world closed in 1971.



Today the ammonia industry is restructuring itself in order to recover from an oversupply situation. Four U.S. plants were permanently closed in 1999. A combined capacity of 1.2 million tonnes has been eliminated. In order to balance the market, other plants had closed their facilities for periods ranging from 1 to 3 months. Besides, prices of farm products have decreased reducing overall production and fertilizer demand. Ammonia prices will probably continue to decline until more high-cost facilities close.

According to the Environmental Defense Fund (EDF) 365,000 tonnes (N) of were production related wastes in 1996. From these wastes, 147,000 tonnes (N) are produced by the chemical sector. The rest (217,000 tonnes (N)) is produced by 23 different industries like petroleum, food, primary metal, and paper. Total production-related waste is the sum of all non-accidental waste generated at a facility, prior to any form of on-site or off-site waste management. Some on-site waste management techniques are recycling, treatment, and combustion for energy recovery. Off-site management includes transfers for disposal, treatment, recycling, or energy recovery.

Additionally, 73,000 tonnes (N) were released into the environment. From these, 42,000 tonnes (N) were emitted by the chemical sector while 31,000 tonnes (N) were emitted by other sectors. Total environmental releases includes all reported releases to air, water, and land, but does not include any waste that is transferred off-site. Therefore, it does not include any environmental releases that may occur from off-site disposal or treatment. Thus, the total amount of ammonia lost in 1996 was approximately 438,000 tonnes (N).

¹ Miscellaneous consider household cleaning agents, industrial refrigerants, metallurgy, pulp reduction, and NO_x reduction equipment.

II. Ammonia's Derivatives

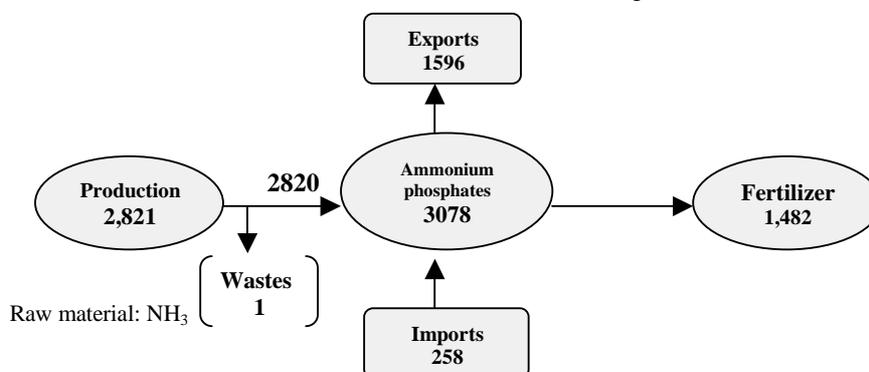
1. Ammonium Phosphates

Ammonium phosphates constitute a large class of fertilizers produced from phosphoric and anhydrous ammonia. It is extensively used in liquid fertilizers; and is also available in granular form. Animal feed and industrial uses are relatively minor.

The United States produces about 40% of the total world output of these compounds and it dominates world exports with more than 50% [iii]. Exports are strong due to a heavy demand in Asia and the Pacific Rim, and an increasing market to Europe. According to the U.S. Bureau of Census, the amount of ammonium phosphates produced in 1996 was 16,900,000 tonnes, or 2,820,000 tonnes of contained nitrogen.

Total exports were 1,596,000 tonnes (N). Of this 1,430,000 tonnes (N) were diammonium phosphate and 166,000 tonnes (N) were monoammonium phosphate. Meanwhile, imports amounted to 258,000 tonnes (N), 77,000 tonnes (N) of diammonium phosphate and 181,000 (N) of monoammonium phosphate [iv]. Thus the apparent consumption of ammonium phosphates for 1996 was 1,482,000 tonnes (N) (see Figure 3).

Figure 3. Ammonium Phosphates Consumption in the United States in 1996
(Thousand metric tons of contained nitrogen)

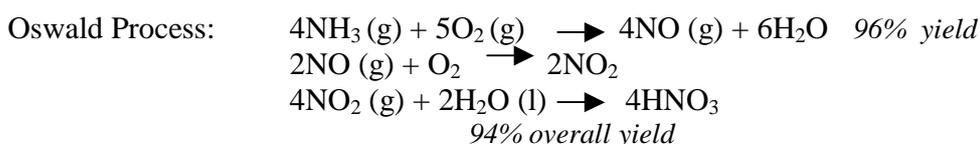


Source: Kramer, U.S. Geological Survey, 1997

Ammonium phosphates are produced by reacting phosphoric acid (H₃PO₄) with anhydrous ammonia (NH₃). According to the EPA 0.07 kg of ammonia is lost per tonne of product. Therefore, for total ammonium phosphates production (16,911,000 tonnes gross weight), 972 tonnes (N) of ammonia are lost.

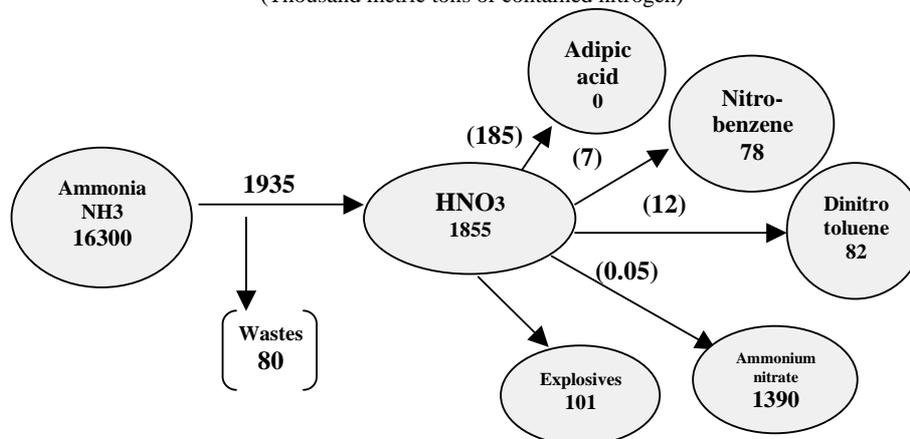
2. Nitric Acid

Nitric acid is an extremely important intermediate chemical used in the manufacture of fertilizers and explosives. It is made from ammonia using the Oswald Process; where O_2 and NH_3 react together at a high temperature and pressure, then oxidized to NO_2 and dissolved in water to make HNO_3 . The biggest (80%) use of nitric acid is in making ammonium nitrate. Other important end uses for nitric acid are as intermediates in the production of fibers, plastics, elastomers, and explosives.



As shown in Figure 4, total production of nitric acid in the U.S. in 1996 was 8,350,000 tonnes; of which 1,855,00 tonnes were contained nitrogen [v]. World trade in this material is minimal. Since there is no available information on U.S. imports and exports, production is assumed to be equal to consumption.

Figure 4. Nitric Acid Consumption in the United States in 1996
(Thousand metric tons of contained nitrogen)



According to the Environmental Protection Agency, 33,692 tonnes (N) of nitrous oxides were emitted to the atmosphere due to nitric acid production in 1996; roughly 3% of U.S. emissions of N_2O [vi]. It is important to keep track of nitrous oxide emissions because they contribute to the greenhouse effect. Although actual emissions of this compound are much smaller than CO_2 emissions, over a 100-year time horizon, N_2O is 270 times more potent than CO_2 per unit mass at absorbing and trapping heat [vii].

Human activities have increased atmospheric concentrations of N_2O by 8% over the past two hundred years. According to the EPA, the principal activities producing N_2O are soil management and agricultural fertilizers, accounting for 71% of total emissions. As shown in Table 1, the remaining 29% is composed of fossil fuel combustion (20%), adipic acid production (5%), and agricultural waste burning (1%) [viii].

Table 1. Principal Activities Producing N₂O

Activity	N₂O Contribution
Soil management and fertilizer use	71%
Fossil fuel combustion	20%
Adipic acid production	5%
Nitric acid production	3%
Agricultural waste	1%

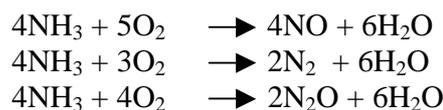
Source: EPA, 1999

NO and NO₂ (or NO_x) are also emissions from nitric acid production that are regulated by the U.S. government. There are basically four processes for NO_x abatement: extended absorption with water, non-selective catalytic reduction, selective catalytic reduction, and absorption in sodium hydroxide solution. Most of the old plants use non-selective catalytic reduction. This method has the advantage of reducing N₂O emissions as well; however, newer plants did not adopt it because it requires high temperatures and pressures. In addition, there is no regulation of N₂O emissions in nitric acid plants.

The reason why NO_x is regulated is because it contributes to ground-level ozone formation that can cause severe respiratory problems. It reacts to form nitrate (-NO₃) particles and contributes to the formation of acid rain and eutrophication of rivers. NO_x reacts with organic compounds including ozone to form toxic chemicals in the atmosphere and causes visibility impairment.

Emissions coefficient range from about 0.97 to 19.35 kg of NO_x/tonne of nitric acid and approximately 2.91 to 33.97 kg of N₂O/tonne of nitric acid [ix]. However, the Department for Natural Resources and Environmental Protection has established an emission limit for NO_x of 2.9 kg/tonne of nitric acid. This would total 5,380 tonnes of NO_x or about 1,637 tonnes of contained nitrogen supposing that all facilities respect the regulation. Actual emissions are likely to have been much larger.

During the Oswald Process some pure nitrogen (N₂) is formed as well. To determine the amount of nitrogen lost in the form of N₂, a simulation of the first stage of the Oswald Process was developed using Aspen PlusTM. The chemical reactions used were the following:



Other parameters used for the simulation based on information from the European Fertilizer Manufacturers Association were as follows: a yield of 96% NO, temperature range of 810-850 °C, and pressure from 1.7 to 6.5 bar. With such conditions, the results obtained using the model RSTOIC are presented in Table 2:

Table 2. Results of the Simulation of NO Production (Stage One of the Oswald Process) Using Aspen PlusTM

	Reactants Stream	Products Stream
Temperature (C)	100	875
Pressure (bar)	1.013	2
Mass Fraction:		
NH ₃	0.299	Trace
O ₂	0.701	0.020
NO		0.476
H ₂ O		0.474
N ₂		0.012
N ₂ O		0.018

Since this is the only reaction in the entire Oswald Process where N₂ is formed, the above simulation is sufficient to estimate the production of N₂ using its production mass fraction in proportion to N₂O's mass fraction. As a result, the amount of N₂ generated as a by-product in 1996 is estimated at 44,341 tonnes. Overall waste production is estimated at 79,670 tonnes of contained nitrogen for the production of nitric acid (see Table 3).

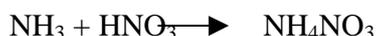
Table 3. Waste Products of Nitric Acid Production in 1996

Compound	Amount (tonnes)
N ₂ O	33,692
NO _x	1,637
N ₂	44,341
Total	79,670

Moreover, according to TRI in 1996 about 18,000 tonnes (N) were production related wastes and 2,000 tonnes (N) were released into the environment by the chemical industries. Additionally, the rest of the industrial sectors released about 200 tonnes (N). An important amount of nitric acid can be recuperated and recycled and the rest should be neutralized before dumping. However, the environmental releases are mostly lost through evaporation or water disposals and do not receive any treatment.

2.1 Ammonium Nitrate

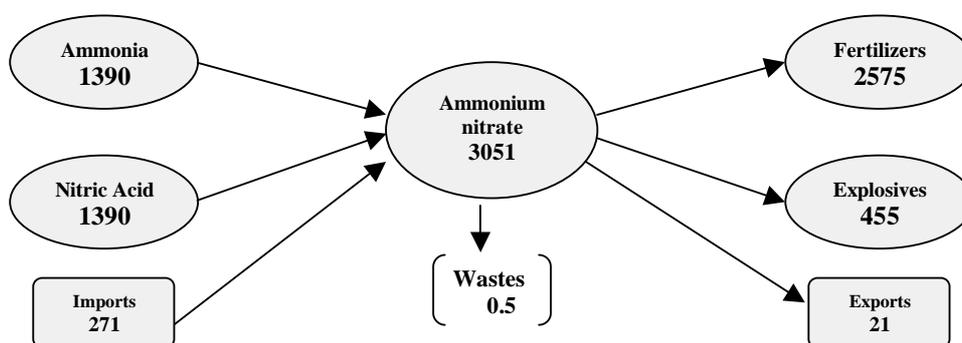
Ammonium nitrate is one of the most important products of nitric acid. It is used both as a fertilizer and as an industrial explosive in mining. This compound is prepared by neutralization of nitric acid with ammonia in the following reaction:



According to the U.S. Bureau of Census in 1996 the amount of ammonium nitrate produced was 2,780,000 tonnes contained nitrogen. Net imports were 271,000 tonnes, while net exports were 21,000 tonnes.

Consequently, 1,390,000 tonnes (N) of nitric acid and an equal amount of contained nitrogen in the form of ammonia were used to produce ammonium nitrate, representing 75% of the total nitric acid production. According to SRI, it is estimated that industrial uses for this compound are about 10- 15% of the market. Its primary application is as fertilizer. Evidently the amount of ammonium nitrate used as fertilizer is 2,575,000 tonnes of contained nitrogen (see Figure 5).

Figure 5. Ammonium Nitrate Consumption in the United States in 1996
(Thousand metric tons of contained nitrogen)



Ammonia and nitric acid are virtually required in stoichiometric quantities for the production of this compound. No by-products or co-products are produced. But an ammonium nitrate plant may emit ammonium nitrate, ammonia, and nitric acid. According to the European Fertilizers Manufacturer's Association, the BAT (Best Available Technology) emission levels are 0.2 kg ammonia per tonne of product and 0.22 kg (N) of ammonium nitrate per tonne of product. This is considering that any excess nitric acid is neutralized into ammonium nitrate. The minimal quantity of emissions is 520 tonnes (N). The actual loss is probably several times as large.

2.2 Explosives

The U.S. Bureau of Census reported production of 2,240,000 tonnes of all kinds of industrial explosives in 1996. However, the exact composition of the explosives' mixture was not determined. Table 4 shows the classification system used: permissibles, other high explosives, and blasting agents.

Of the total amount of explosives produced, 2,510 tonnes were permissibles and 31,800 tonnes were other high explosives. The rest were 2,200,000 tonnes of blasting agents (see Table 5).

The principal non-military use of explosives is for the coal mining industry, consuming 65% of the whole production. Quarrying and non-metal mining consume 14%, and metal mining 11%. Construction work amounts for 7%, and all other purposes 3%.

Table 4. Classification of Industrial Explosives Used by the US Bureau of Census

Classification	Description
High Explosives	
Permissibles	Grades approved by brand name by the Mine Safety and Health Administration, as established by the US Bureau of Mines testing.
Other high Explosives	All high explosives except permissibles.
Blasting agents	Ammonium nitrate-fuel oil; bulk and packaged slurries, water gels, and emulsions; and unprocessed ammonium nitrate.

Source: Kramer, U.S. Geological Survey, 1997

Table 5. Statistics of Industrial Explosives and Blasting Agents Sold for Consumption in the United States
(Tonnes)

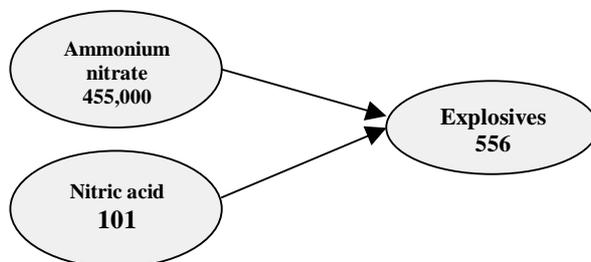
Class	1996 Production
Permissibles	2,510
Other high explosives	31,800
Blasting agents and oxidizers	2,200,000
Total	2,240,000

Source: Kramer, U.S. Geological Survey, 1997

Yet, this information is not enough to determine the nitrogen content in the explosive's mixture. The estimate has to rely on information from its raw materials: ammonium nitrate and nitric acid. Thus, if 15% of ammonium nitrate production was used for preparation of explosives, 455,000 tonnes contained nitrogen of the explosives came from this source. In addition, according to the nitric acid material balance, 102,000 tonnes (N) of nitric acid were used for explosives' production, totaling 557,000 tonnes (N) (see Figure 6). This figure includes military explosives.

**Figure 6. Explosives Consumption in the United States in 1996
(Industrial and Military)**

(Thousand metric tons of contained nitrogen)



Moreover, the total amount of nitrogen contained in explosives is released into the atmosphere the moment they are used. According to the information above, the average nitrogen content in the explosives' mixture is 25%. Table 6 shows compounds synthesized during explosions and the quantities in which they are produced per tonne of explosive detonated. This information was obtained using Aspen PlusTM. The simulations were carried out using RGibbs, which essentially calculates chemical and phase equilibrium by minimizing Gibb's free energy. Conditions used were 1 atm of pressure, since most explosions are carried out in open air, and the heat of detonation of each explosive.

**Table 6. Explosive's Use Emissions
(kg/tonne of explosive)**

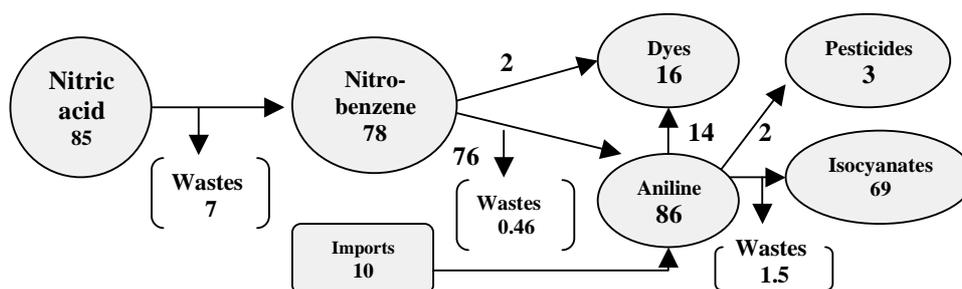
Explosive	CO	CO ₂	H ₂ O	N ₂	NO	N ₂ O	NH ₃	HCN	C ₂ H ₂	CH ₄
Ammonium nitrate	0	0	450	175	375	0	0	0	0	0
TNT	712	0	18	176	0	0	2.6	13	2.56	76
PETN	177	418	228	177	0	0	0	0	0	0
Tetryl	633	0	95	232	0	0	7.2	11.5	0	20
Nitroguanidine	185	0	227	532	0	0	7.8	0.3	0	48
Nitroglycerin	0.08	581	198	123	0	97	0	0	0	0

However, the exact amount of pollutants emitted cannot be determined. And even when we know that 455,000 tonnes (N) of the explosive production came from ammonium nitrate it is rarely used alone. Ammonium nitrate is mostly used either as ANFO (containing 6% fuel oil) or as water gels. In the ANFO case, the addition of carbon to the explosive would generate the production of organic compounds, which would be mostly CO or CO₂. Nevertheless, other organic pollutants could also be generated. It is not possible to run a simulation on this process since the outcome would depend entirely on the composition and quality of the fuel oil used.

2.3 Nitrobenzene

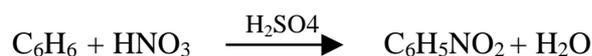
According to ChemExpo the amount of nitrobenzene demanded in 1997 was 725,760 tonnes with a historical growth of 5% per year (1988-1997). Therefore, demand estimation of nitrobenzene in 1996 was 689,000 tonnes. Given that the chemical formula for this compound is C₆H₅NO₂ and its molecular weight is 123.11, which is 11.37% contained nitrogen. Overall consumption results in 78,000 tonnes (see Figure 7).

Figure 7. Nitrobenzene Consumption in the United States in 1996
(Thousand metric tons of contained nitrogen)



The main use for nitrobenzene is aniline, which accounts for 97% of production. Expected future growth will be above average due to strong demand for MDI-based polyurethanes.

Nitrobenzene is produced by a highly exothermic reaction. In this reaction benzene and nitric acid are reacted in the presence of sulfuric acid. About 5% of benzene production is used for producing nitrobenzene and most of nitrobenzene's processes use a series of continuous stirred-tank reactors. Nitration usually occurs at 55 °C and 1 atm of pressure according to the following reaction:



After the nitration process, benzene is separated from the aqueous waste using a decanter. Then, crude nitrobenzene is washed and neutralized. The washer and neutralizer effluent is then sent to a wastewater treatment. The residual aqueous acidic wastes are denitrated using fresh benzene. About 7,000 tonnes (N) of nitric acid are production-related wastes according to the material balance. Nitrobenzene is extracted from sulfuric acid, which was used as a catalyst, and excess benzene is recovered through distillation. Stripped sulfuric acid used is either recycled into the process or sold.

Emissions of nitrobenzene are likely to occur both during production and use. However, since it is mostly used in the production of aniline and the number of aniline and nitrobenzene plants is limited, industrial emissions are fairly localized. According to the U.S. Toxics Release Inventory (TRI), production related wastes of nitrobenzene are estimated at 3,765 tonnes/year [x]. This represents 428 tonnes (N). According to TRI, approximately 36 tonnes (N) are released into the environment each year. However, since many major industries are not covered by TRI the release information often substantially underestimates actual environmental releases.

2.4 Aniline-A

ChemExpo reports that the amount of aniline consumed in 1997 was 607,824 tonnes. Considering a historical growth of 5.4 % per year (1988-1997), demand production for 1996 can be estimated at 575,000 tonnes.

The chemical formula of aniline is C₆H₇N and its molecular weight is 93.128; which is 15% contained nitrogen. Thus, total nitrogen embodied in aniline in 1996 was 86,440 tonnes. However, the production of nitrobenzene was only 78,405 tonnes of which 2,000 were used for dyes, rubbers, and other chemicals. To provide 86,440 tonnes of aniline, imports had to add 9,603 tonnes (N). Main uses of aniline are described in Table 7.

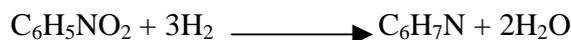
Table 7. Main Uses for Aniline

P, p -methylene diphenyl diisocyanate	80%
Rubber-processing chemicals	11%
Herbicides	3%
Dyes and pigments	3%
Specialty fibers	2%
Miscellaneous*	1%
*Includes explosives, epoxy curing agents, and pharmaceuticals	

Source: ChemExpo, February 8, 1999

The main derivative of aniline is p,p-methylene diphenyl diisocyanate (MDI), which is used in production of polyurethanes and other plastics. Due to its increasing use in housing and automotive parts, a demand growth for aniline is expected in future years. Actually, domestic demand is expected to grow at an annual rate of 6% even though its use as an herbicide is declining. In both rubber chemicals and agricultural chemical uses, the importance of aniline is considerable.

Aniline is produced commercially by catalytic reduction of nitrobenzene. This is mostly done through hydrogenation of nitrobenzene at temperatures below 350 °C using a catalyst. The chemical reaction is the following:



According to the Environmental Protection Agency, 93,895 tonnes (N) of aniline were produced and 109 tonnes (N) aniline were released in 1992. If we consider the releases to be proportional to production, the 1996 releases of aniline would have been about 100 tonnes. However TRI estimates tend to be too low, where actual emissions may be considerably larger.

When aniline is released to air it reacts with any free radical and undergoes direct photolysis. The half-life of atmospheric aniline has been estimated at 3.3 hrs. If released to soil, aniline will degradate into CO₂. The half-life of this process is 4 days. Finally, if it's released to water it's subject of biodegradation, photo-degradation, and adsorption to sediment and humus. According to the Environmental Defense Fund 1,537 tonnes (N) were product related wastes in 1997 or 1,455 tonnes (N) for 1996.

2.5 Toluene Diisocyanate

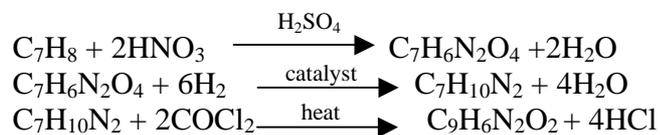
Demand for toluene diisocyanate in 1998 was 426,384 tonnes. The historical growth from 1989 to 1998 has been 2.7% per year. Thus, demand during 1996 was 403,000 tonnes including exports of 131,000 tonnes. The chemical formula is $C_9H_6N_2O_2$ and its molecular weight is 174.16. Therefore, the amount of contained nitrogen was about 65,000 tonnes including exports of 10,000 tonnes. The main use for toluene diisocyanate is in flexible urethane foam; some other uses are presented in Table 8.

Table 8. Main Uses for Toluene Diisocyanate

Flexible urethane foams	90%
Polyurethane coatings	4%
Cast elastomers	2%
Sealants	2%
Miscellaneous, including polyurethane fibers	2%

Source: ChemExpo, April 12, 1999

Production of toluene diisocyanate (TDI) is carried out in two stages by nitration of toluene using nitric acid, in the presence of sulfuric acid, resulting in dinitrotoluene. Afterwards, dinitrotoluene is reacted with hydrogen to produce toluenediamine. This is then phosgenated; that is, reacted with phosgene ($COCl_2$) to produce toluene diisocyanate. TDI is produced by the following reactions:



According to the Environmental Defense Fund, in 1997 the amount of process related wastes of toluene diisocyanate were 8,236 tonnes or 1,324 tonnes (N). In addition 66,145 tonnes (N) were produced the same year. In proportion, estimate waste production in 1996 was 1,300 tonnes. EPA states that there is a great concern over toluene diisocyanate emissions as a potential carcinogen and as potentially provoking dermal and pulmonary sensitization.

2.6 Dinitrotoluene

Nitration of toluene results in the formation of dinitrotoluene in its various isomeric products. These are used as intermediates for the production of toluene diisocyanate, dyes, and explosives. Yet, its main use is in the production of toluene diisocyanate; with very small quantities used for other purposes.

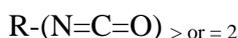
According to the material balance, to produce 64,840 tonnes (N) of toluene diisocyanate it is required at least the same molar amount of dinitrotoluene plus whatever is lost during the process. Spectrum Laboratories reports that to produce 40,838 tonnes (N) of toluene diisocyanate, 51,600 tonnes (N) of dinitrotoluene are needed. Therefore, extrapolating, for 64,840 tonnes (N), 82,000 tonnes (N) of dinitrotoluene would be necessary. This will produce an overall loss of 17,087 tonnes (N) of dinitrotoluene.

There is not much literature available for dinitrotoluene production processes. However, dinitration can be done in one or two steps and in batch or continuous fashion. The first nitration is done easily but the second has to be forced using different mixtures of nitric and sulfuric acids.

Nevertheless, due to regulations as well as economical reasons most of the sulfuric acid is recovered and the nitric acid neutralized. This is done using a series of separation columns as well as washing tanks, evaporators, filtration units, and distillation units. But, according to the material balance approximately 12,000 tonnes (N) of nitric acid are lost during the process. Some of it might be recovered and the rest could be neutralized. Furthermore the Environmental Defense Fund states that 355 tonnes or 55 tonnes (N) of dinitrotoluene are released into the environment each year.

2.7 Isocyanates

An isocyanate is any chemical substance that contains two or more isocyanate functional groups (-N=C=O). (Substances containing precisely two isocyanate groups are known as diisocyanates.)



Isocyanates can be produced by several methods, but the most common one is the phosgene-based process already described for toluene diisocyanate production. Production of any isocyanate monomer is represented by the following formula:

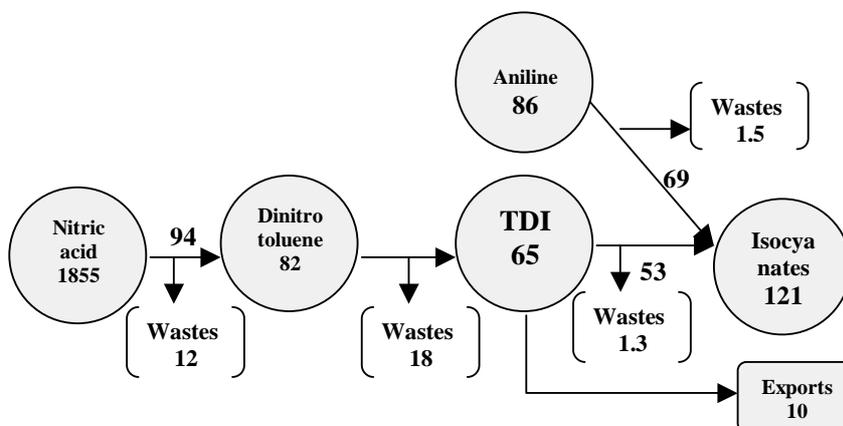


The main problem with this method is the enormous amount of hydrochloric acid produced, which is a hazardous chemical. Further, since phosgene is highly toxic and reactive, diligent care and precautions are required.

Toluene diisocyanate (TDI) and PMDI are the most widely used isocyanates in the manufacture of urethane polymers and plastic foams. PMDI is a polymer isocyanate obtained by the phosgenation of aniline-formaldehyde-derived polyamines.

Total production of isocyanates was 123,521,000 tonnes in 1996. Of this, 54,369,000 tonnes were toluene diisocyanate, while 69,152,000 tonnes came from aniline derivatives (see Figure 8). The largest market for these products is in the furniture and bedding industry. However, these compounds are also used widely in other plastic products.

Figure 8. Isocyanates Consumption in the United States in 1996
(Thousand metric tons of contained nitrogen)



2.8 Adipic acid

According to Chemexpo, 889,000 tonnes of adipic acid were produced in 1997. Based on historical growth of 2% per year (1988-1997), 1996 production is estimated at 871,000 tonnes. Imports amounted to 50,000 tonnes while exports were 59,000 tonnes. Even though adipic acid does not contain nitrogen in it, an enormous quantity of N is lost during its process.

Adipic acid is produced commercially through nitric acid oxidation of a cyclohexanone-cyclohexanol mixture called KA oil (ketone-alcohol). This process is done in two consecutive major reactions. First, cyclohexane is oxidized to produce cyclohexanol. Secondly, the KA mixture is oxidized with nitric acid to produce adipic acid. The adipic acid obtained is then separated from the water and the remaining nitric acid, which is recuperated and recycled to the reactor. Finally, adipic acid is dried and cooled before packaging and shipping. Most of the adipic acid production is used in the manufacture of nylon.

Just as in nitric acid production, the U.S. government regulates NO_x emissions from adipic acid. There are four facilities producing adipic acid in the United States and all of them have NO_x emissions controls. EPA monitored these emissions in the three largest ones. Two of them belong to Dupont and the third to Solutia. The fourth plant, Allied-Signal, in Hopewell, Virginia produces about 23,000 tonnes of adipic acid per year. Adipic acid is produced as a by-product of their caprolactam plant. According to EPA, Allied contends that NO_x emissions are low, although no emission test data was provided. Table 9 shows NO_x emission factors for the other three facilities.

The total amount of emissions for 1996 was calculated supposing that production in each facility was equal to full plant capacity. Total production capacity for the three facilities is around 850,000 tonnes, while internal demand amounted to 871,000 tonnes (plus 50,000 tonnes that were imported). The Allied-Signal plant has a capacity of

approximately 23,000 tonnes. This will give an overall capacity of 873,000 tonnes, which is practically equal to demand. Besides, Dupont's and Solutia's expansion plans suggest that they are already working very close to full capacity. According to Chemexpo, Dupont is in initial phases of an expansion program that will add approximately 150,000 tonnes of adipic acid to three of its facilities (one of them in Canada). On the other hand, Solutia has been adding capacity to its adipic acid plant due to a new phenol unit that will be completed this year.

Table 9. NO_x Emissions from Adipic Acid Facilities in the U.S.

Plant	Capacity (tonnes)	NO _x Emission factors ^a (kg NO _x /tonne adipic acid)	NO _x Emissions in 1996 (tonnes)
A ^b	200,000	3.7	740
B ^b	350,000	4.7	1,645
C ^c	300,000	1.7	510
		Total	2,895

a Source EPA, 1991

b Monitoring conducted in 1989

c Monitoring conducted in 1976. Recent data is not available.

The approximate amount of NO_x emitted in all three facilities is 2,895 tonnes (see Table 9). If the mixture of NO/NO₂ can be estimated at 75% NO and 25% NO₂, the overall nitrogen content of the mixture would be 1,230 tonnes.

However, just as in nitric acid production N₂O is also a major emission in adipic acid facilities. According to Thiemens and Trogler, one mole of N₂O is produced per mole of adipic acid [xi]. The molecular weight of adipic acid is 146.14 and for nitrous oxide is 44.0128. Thus, for 871,000 tonnes of adipic acid, 262,000 tonnes of nitrous oxide or 184,000 tonnes (N) are generated. This accounts 184,000 tonnes (N) of nitric acid in 1996.

However, not all of the produced N₂O reaches the atmosphere. There are some companies that treat emissions in a reductive furnace, which turns N₂O into N₂. According to EPA in 1996, U.S. adipic acid production emitted 73,000 tonnes of nitrous oxide. This represents 5% of the total N₂O emissions. All adipic plants in the U.S. were supposed to have N₂O control systems by 1996; however, only half of them had controls operating by then [xii]. Therefore, overall wastes for adipic acid production are 184,000 tonnes (N) as N₂O (however an important part is reduced to N₂) plus 1,230 tonnes (N) as NO_x, totaling 185,230 tonnes (N). Other important wastes for this process are CO and CO₂.

3. Urea

The chemical formula for urea is $\text{CH}_4\text{N}_2\text{O}$, which is 46.62% (N). Its molecular weight is 60.055. According to the Chemexpo Chemical Profile, the capacity for urea production within the United States is 8,794,000 tonnes/year. However, the United States Bureau of Census reports that 7,740,000 tonnes, or 3,550,000 tonnes (N), were produced. Exports for 1996 amounted to 675,000 tonnes (N) and imports to 1,170,000 tonnes (N). Thus, the total quantity of nitrogen consumed was 4,045,000 tonnes (N) (see Figure 9).

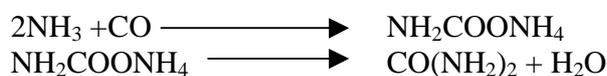
Out of the 4,045,000 tonnes consumed within the U.S., the usage distribution was the following: 3,221,000 tonnes used as fertilizer, 283,000 tonnes as livestock feed, 166,000 tonnes as melamine, 52,000 tonnes as miscellaneous, 202,000 tonnes as resins, and 121,000 tonnes lost (see Table 10). Most of the solid urea produced as prills and granules, is used as fertilizer, protein supplement in animal feed, and in the manufacture of plastics.

Table 10. Main Uses for Urea

Fertilizer, including solid and nitrogen solutions	80%
Livestock feed	7%
Urea-formaldehyde resins	5%
Melamine	4%
Miscellaneous ^a	1%
Lost ^b during transportation, storage, and conversion into downstream products	3%
a Includes cyanuric acid for chlorinated isocyanurates; crystalline adducts; deicing agents; pharmaceutical intermediaries, and sulfamic acid, and its ammonium salt.	
b During transportation, storage, and conversion into downstream products.	

Source: ChemExpo, August 11, 1997

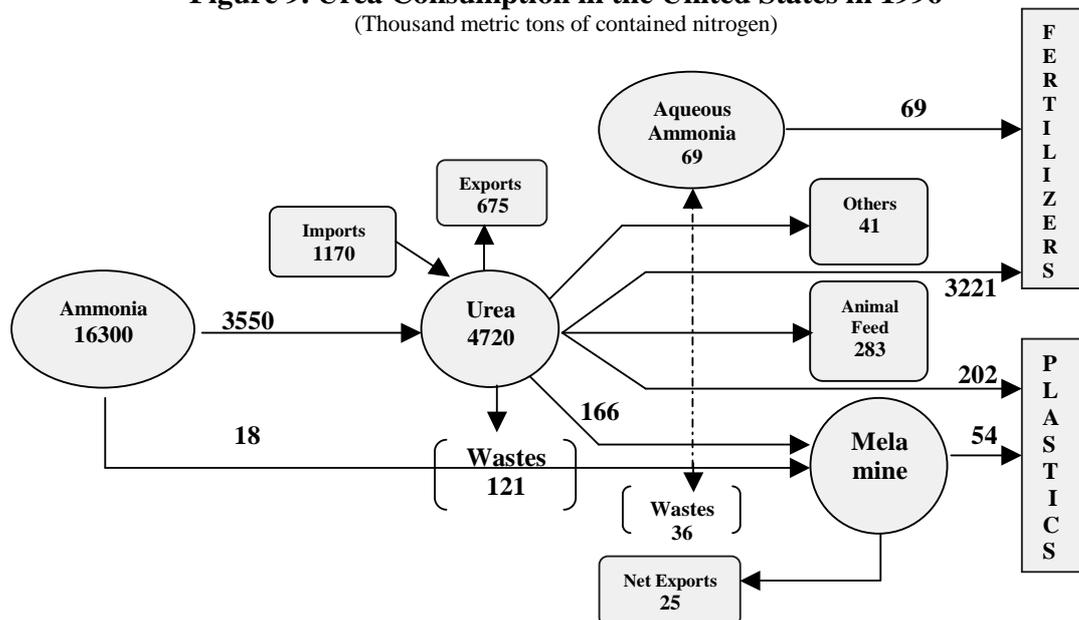
Urea is produced from liquid ammonia and gaseous CO_2 at high temperature and pressure. The formation of ammonium carbamate and the dehydration to urea take place simultaneously. The reactions involved are the following:



The first reaction is very fast and exothermic and goes to completion easily. The second reaction is slower and endothermic. Conversion rate is usually between 50-80% and increases with increasing temperature. Emissions from manufacture are mainly ammonia and particulates.

Figure 9. Urea Consumption in the United States in 1996

(Thousand metric tons of contained nitrogen)



3.1 Melamine

The demand for melamine, reported by the Chemexpo Product Profile, was 117,900 tonnes in 1996. According to ChemExpo, the U.S. annual exports for melamine production have averaged one third or more of its production. For 1996 exports were approximately 37,000 tonnes of melamine representing about 25,000 tonnes (N). This results in an internal consumption of 81,000 tonnes. The chemical formula of melamine is $C_3H_6N_6$, 66% (N) its molecular weight is 123.12. Thus the nitrogen consumption was 78,500 tonnes (see Figure 9).

Table 11. Main Uses for Melamine

Surface coatings	37%
Laminates	32%
Molding compounds	7%
Wood adhesives	6%
Paper coatings	6%
Textile treatment	4%
Miscellaneous, including flame retardants and leather tanning	8%

Source: ChemExpo, October 14, 1996

Melamine is a thermosetting plastic, also called aminoplast. It is comparatively light-weight and strong. Also, it can resist acids and alkalis. Melamine has been produced industrially since 1930, and is used in production of laminates, cooking utensils, electrical appliances, and insulators (see Table 11). Its demand is likely to grow in proportion to the demand of flame-retardant foams for furniture. Its use as a surface coating depends entirely on the rate of new car production.

Formerly melamine was manufactured using heat by the conversion of dicyandiamide. Today it is prepared by dehydration condensation of urea. The process involves about 1.4 kg N-input of urea and 0.2 kg of anhydrous ammonia per kg melamine [xiii]. The difference between input and output nitrogen is recycled as aqueous ammonia.

3.2 Aqueous Ammonia

According to the Fertilizers Institute and the Association of American Plant Food Control Officials, the amount of aqueous ammonia produced in the United States in 1996 was 69,000 tonnes (N). Aqueous ammonia is used mostly in fertilizer products. One of its most important uses is as a nitrogen source in the cultivation of yeast.

4. Ammonium Sulfate

Ammonium sulfate can be produced as a primary product or as a by-product of caprolactam production. According to the US Bureau of Census, production of ammonium sulfate in 1996 was 512,000 tonnes (N). Moreover, 222,000 tonnes (N) were exported and 79,000 tonnes (N) were imported. This results in an apparent consumption of 369,000 tonnes (N).

There are four processes for the production of ammonium sulfate. In the first, it is synthetically manufactured, which is done by combining anhydrous ammonia and sulfuric acid in a reactor. In the second, it is produced as a by-product of caprolactam oxidation process. Third, ammonium sulfate is a by-product of methyl methacrylate (MMA) production. In the last process, ammonium sulfate is produced as a coke oven by-product. However, in this study coke oven by-products are not taken into account because it is not included in official statistics. The reaction for the synthetic production is the following:



According to two different facilities (FACT² Caprolactam Plant and Thai Caprolactam Public Company Limited), caprolactam production accounts for caprolactam represents approximately 25% of total ammonium sulfate produced as by-product. Based on this relationship, ammonium sulfate produced this way is estimated at 344,000 tonnes. From MMA production, 94,000 tonnes (N) were obtained. Thus, ammonium sulfate produced as a primary product is estimated at 74,000 tonnes (N) (see Figure 10).

Ammonium sulfate is used for fertilizers and for industrial purposes. The IFA Data Bank reports that 233,500 tonnes (N) of ammonium sulfate were used as fertilizer in 1996 [xiv]. Evidently 135,000 tonnes were used in other industrial processes.

² Fertilizers and Chemicals Travancore Ltd located in Kerala, South India

5. Caprolactam

ChemExpo reports that 712,140 tonnes of caprolactam were produced in 1997 with a historical growth of 2.3 % per year. With this information, the estimation for caprolactam consumption in 1996 was of 695,760 tonnes and imports totaled 25,402 tonnes (see Figure10).

The chemical formula for caprolactam is $C_6H_{11}NO$ and its molecular weight is 113.16; thus the percentage of nitrogen contained is 12.37. As a consequence, caprolactam consumption was 86,080 tonnes (N) and imports 3,142 tonnes (N). The main uses for caprolactam are presented in Table 12.

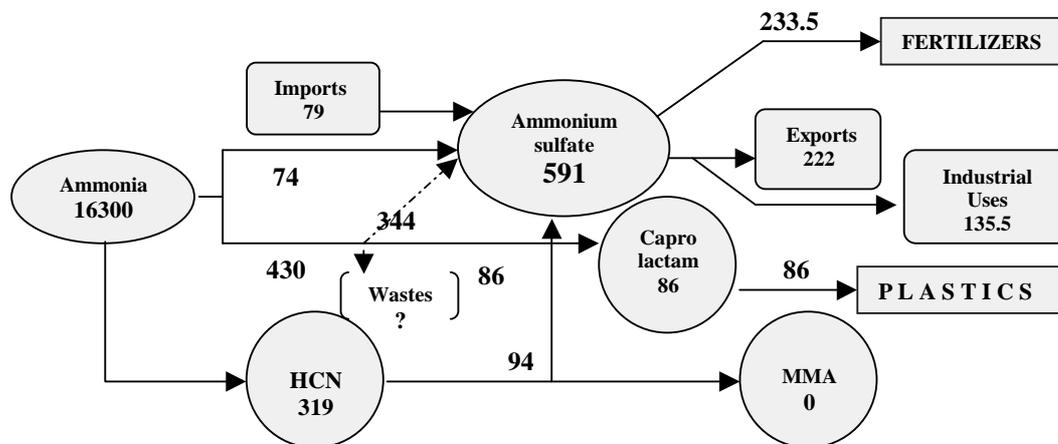
Table 12. Main Uses for Caprolactam

Nylon 6 fibers, including monofilament	80%
Engineering resins and film	20%

Source: ChemExpo, October 14, 1996

Figure 10. Ammonium Sulfate and Caprolactam Consumption in the United States in 1996

(Thousand metric tons of contained nitrogen)

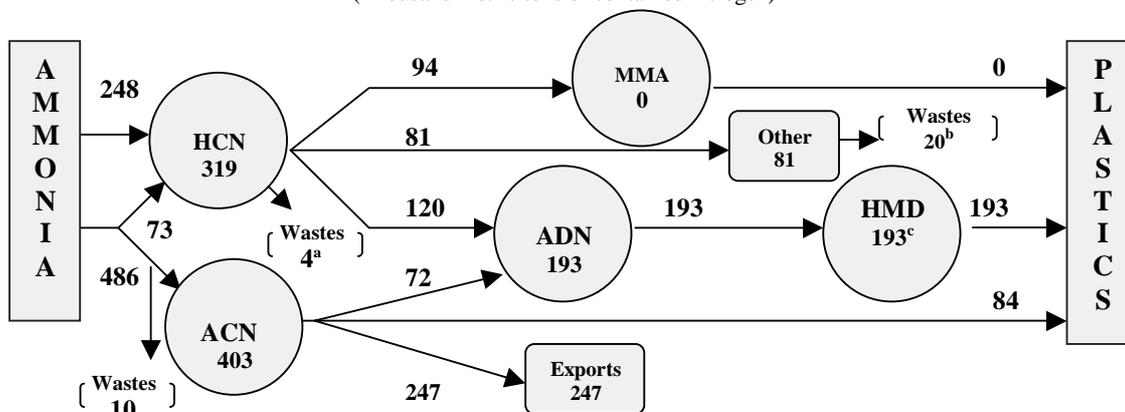


6. Hydrogen Cyanide

According to ChemExpo, the demand for hydrogen cyanide in 1997 was 635,029 tonnes with a historical growth of 3% per year. From this information we estimate the demand in 1996 was 615,978 tonnes. Considering that the chemical formula of the compound is CHN and its molecular weight is 27.026, demand for hydrogen cyanide would be 319,088 tonnes (N). Today, total production capacity in the U.S. is approximately 828,713 tonnes or 429,289 tonnes (N) (see Figure 11). Main uses for HCN are presented in Table 13.

Figure 11. Hydrogen Cyanide and Acrylonitrile Consumption in the United States in 1996

(Thousand metric tons of contained nitrogen)



- ^a HCN emissions reported under HCN production include emissions for other production processes because most facilities that produce HCN also produce HCN sub-products.
- ^b Major producers of wastes are iron and steel production, carbon black and carbon fiber production, and petroleum refineries. However, these estimates are for only 11% of the facilities. There is no basis to estimate emissions from the other facilities.
- ^c There is no available information on the production of Hexamethylenediamine; however, the upper limit of production is given by the amount of adiponitrile produced.

Table 13. Main Uses for Hydrogen Cyanide

Adiponitrile (for nylon 6/6)	41%
Acetone cyanohydrin (for methyl methacrylate)	32%
Sodium cyanide	14%
Methionine	4%
Chelating agents	3%
Miscellaneous, including cyanuric chloride nitrilotriacetic acid and salts	6%

Sources: ChemExpo, November 23, 1998

Hydrogen cyanide can be produced using any of the three following methods. The first one, which is the most widely used (74%), is the Andrussov process [xv] with 236,000 tonnes (N) of HCN. In this process, ammonia, methane and air are reacted over a platinum/rhodium catalyst at a reaction temperature of 1,100 °C. The reaction is the following:



The second method is the Blausaure Methane Anlage Process (BMA). However, it is only used by one facility, which barely accounts for 3% of the HCN production [xvi] or 10 tonnes (N) HCN. In the BMA method, only methane and ammonia are supplied to the reactor. The advantage of this method is that it achieves higher yields of HCN and a relatively pure hydrogen by-product stream. The reaction is the following:



The third source is as a by-product of acrylonitrile, accounting for 23% of the overall production. This process will be further discussed in the adiponitrile section. The secondary reaction in the process producing HCN is the following:



In 1991, HCN emissions reported by producers were 154 tonnes of which 35.5 tonnes came from the adiponitrile plants. If the production in 1991 was approximately 520,733 tonnes of HCN, extrapolating emissions in 1996 can be estimated at 177 tonnes. However, the Environmental Defense Fund reports a total production-related waste of 48,445 tonnes for this compound for 1997. This represents 24,295 tonnes (N) for 1996 and accounted environmental emissions are 394 tonnes (N) for the same period.

Hydrogen cyanide is a poisonous liquid that is emitted from a number of industrial processes such as production of: sodium cyanide, potassium cyanide, adiponitrile, acetone cyanohydrin, cyanuric chloride, and chelating agents [xvii].

6.1 Methyl methacrylate

ChemExpo reports that demand for methyl methacrylate (MMA) in 1997 was 653,184 tonnes with a historical growth (1989-1998) of 2% per year. Therefore, the demand for 1996 can be estimated at approximately 640,120 tonnes. Its chemical formula is $\text{C}_5\text{H}_8\text{O}_2$. However, about 102,108 tonnes of hydrogen cyanide (N) were used in its production. The remaining nitrogen was recycled to ammonium sulfate production (see Figures 9 and 10).

As seen in Table 14, the principal application for methyl methacrylate is the production of acrylic plastics and resins for sheeting and molding compounds. These are used in the automotive industry, construction, and several other industrial applications. Another important end uses are light fixtures, glazing and reflecting signs.

Table 14. Main Uses for Methyl Methacrylate

Acrylic plastics and resins	47%
Surface coatings	24%
Impact modifiers	13%
Emulsion polymers	8%
Mineral-based sheet	3%
Higher methacrylates	2%
Polyester modifiers	2%
Miscellaneous	1%

Source: ChemExpo, June 28, 1999

There is no atmospheric monitoring information for this compound but a certain number of industries report their emissions to the Toxic Chemical Releases Inventory. The amount reported in 1992 was 1,270 tonnes. Therefore, assuming emissions to be proportional to production, approximate emissions in 1996 were 1,423 tonnes MMA. Actual emissions are likely to have been much larger than reported releases.

7. Acrylonitrile

Acrylonitrile is one of the most important sub-products of ammonia. Its chemical formula is C₃H₃N and its molecular weight is 53.063. According to ChemExpo, 1,528,606 tonnes were produced in 1996; since the weight of nitrogen is 26.38% of its molecular weight, the amount of contained nitrogen was 403,246 tonnes (see Figure 11).

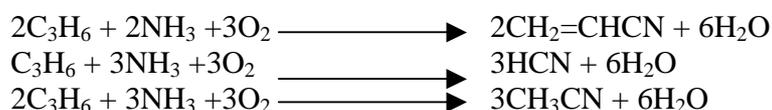
The United States is the largest exporter of acrylonitrile. It supplies 46% of the world exports. In 1996, the total amount exported was 156,035 tonnes (N). This is about 39% of the domestic production. Main uses of acrylonitrile are adiponitrile production followed by ABS/SANS resins, and acrylic fibers (see Table 15).

Table 15. Main Uses for Acrylonitrile

Adiponitrile	30%
ABS/SAN resins	28%
Acrylic fibers	25%
Acrylamide	6%
Miscellaneous, including, polymers, polyols, barrier resins, and carbon fibers	7%

Source: ChemExpo: July 14, 1997

There are six plants in the United States that produce acrylonitrile. All six of them use the Sohio process. This involves propylene, anhydrous ammonia and air to produce acrylonitrile with HCN and acetonitrile as by-products. Operating conditions are from 35 to 207 kPa and from 400 to 510 °C. The reactions are the following:



Acetonitrile is a by-product of acrylonitrile production. It is used as an extraction solvent for butadiene, for pesticide production, and as a solvent. However, the truth is that around 97% of this substance is released into the environment. The amount of acetonitrile produced in 1992 was 14,700 tonnes while the production of acrylonitrile was 1,394,112 tonnes. Therefore, the production of acetonitrile in 1996 was 15,994 tonnes. This will be around 15,514 tonnes or 5,291 tonnes (N).

On the other hand, according to TRI the amount of acrylonitrile that was released into the atmosphere in 1992 was 2,495 tonnes^{xviii}. Extrapolating, emissions in 1996 were 2,715 tonnes or 916 tonnes (N). However, according to the Environmental Defense Fund 4,142 tonnes (N) were production-related wastes. This represents 4,058 tonnes (N) for the 1996 consumption.

7.1 Adiponitrile

According to ChemExpo, 30% of acrylonitrile is used in adiponitrile production. From 247,000 tonnes (N) consumed, 74,000 were converted into adiponitrile. Moreover, 41% of the consumption of hydrogen cyanide goes directly into adiponitrile, resulting in overall production of 193,000 tonnes (N). Its chemical formula is $\text{NC}(\text{CH}_2)_4\text{CN}$ and its molecular weight is 108.14. Consequently, total adiponitrile production amounted approximately to 745,000 tonnes.

According to Dupont, the primary uses for this compound are intermediate for hexamethylenediamine (used for nylon 6) and adipoguanamine resins

Three facilities produce adiponitrile in the U.S. Dupont owns two of these facilities and Monsanto owns the third one. Monsanto produces adiponitrile from electrohydrodimerization of acrylonitrile. The process used by Dupont is the hydrocyanation of butadiene. In this process, dry butadiene is fed into a reactor along with HCN and a catalyst. The catalyst and unreacted raw material are separated from adiponitrile. However, this method produces HCN emissions. According to the 1991 Toxics Release Inventory (TRI), the amount of HCN released was 35.5 tonnes^{xix}. Extrapolating, the estimate for 1996 is 41 tonnes.

7.2 Hexamethylenediamine

There is no available information on the production of hexamethylenediamine due to the fact that Dupont produces 50% of the world's consumption for this compound. Therefore, the upper limit of production for this compound is the amount of available adiponitrile (193,000 tonnes).

The main use of hexamethylenediamine is in the production of nylon 66, nylon 69, nylon 610, and nylon 12. Furthermore, it can be used as a hardener for epoxy resins, in hexamethylene diisocyanate production, and as accelerator in fluorinated and polyacrylate elastomers vulcanization [30].

Conclusion

The importance of nitrogen-based chemicals is increasing as plastic uses generalize and agricultural needs grow. Ammonia is the starting point for all N-based chemicals because it is the only compound that can be produced using N_2 as raw material.

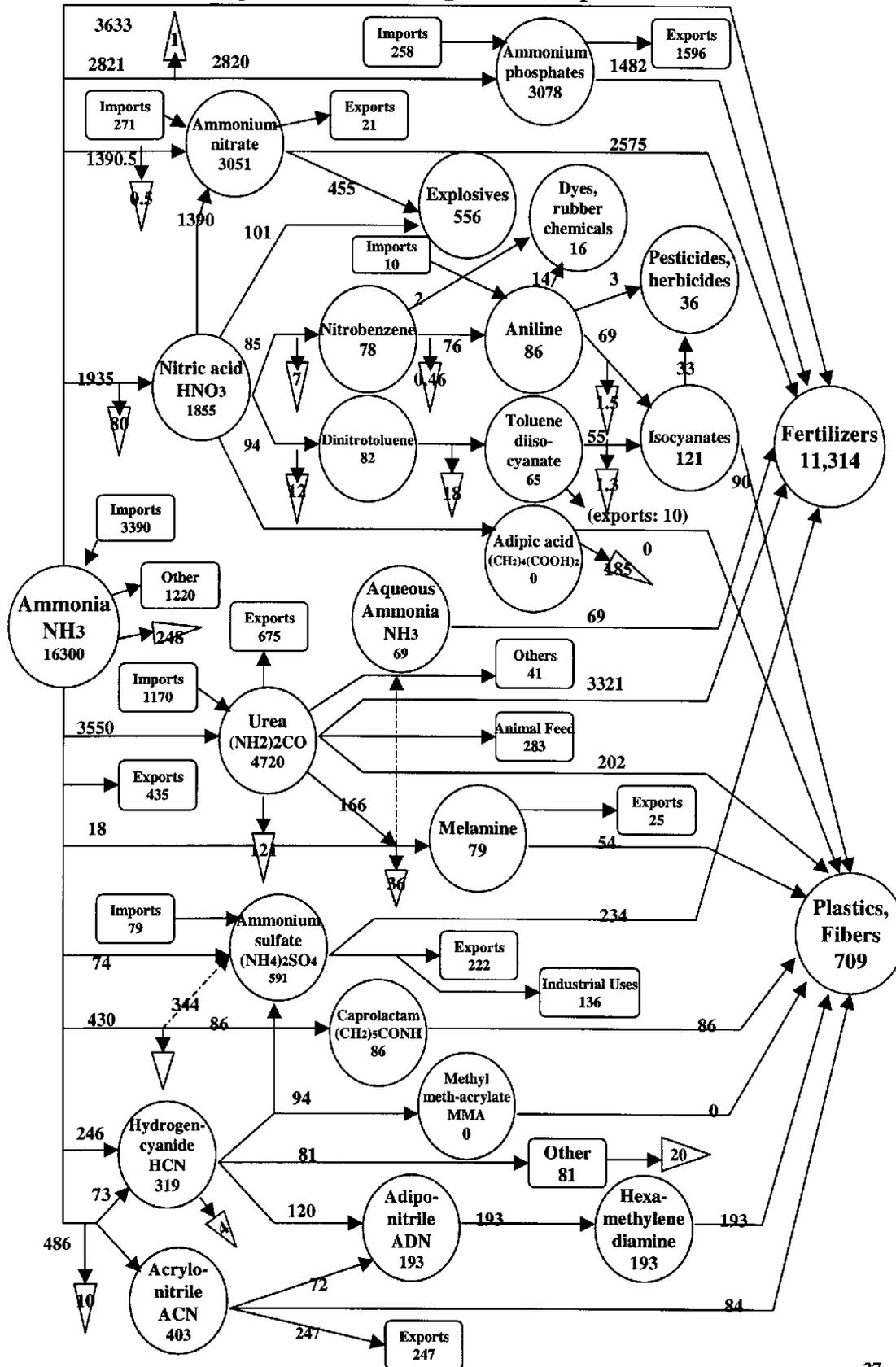
Total U.S. ammonia consumption in 1996 was 15,865,000 tonnes of which 11,314,000 tonnes of nitrogen was used as fertilizer. And this amount will increase every year with population growth. Lakes and rivers eutrophication are already a very serious problem all over the world and it seems it's not going to change. Underground water supplies are also being contaminated by fertilizers and soil acidity provoked by them releases heavy metals in the soil that are washed away by water.

Figure 12 shows the summary of the total material balance for the nitrogen industry. According to this, fertilizers accounts for 78% of total consumption, while plastics and fibers add 5%. Explosives account for 4%. About 4% is spread among animal feed, dyes, rubbers, chemicals, pesticides, and industrial uses. The remaining 9% includes non-miscellaneous uses, undercounts, and losses. Imports of the different nitrogen compounds amounted to 5,178,000 tonnes (N), while exports added up to 3,221,000 tonnes (N).

On the other hand, plastics and fibers production amounted to 709,000 tonnes. However, very important emissions are related to this sector especially in the production of adipic acid, an intermediate in nylon production. Production of adipic acid contributes approximately 5% of all global nitrous oxide emissions. Production of explosives amounted to 556,000 tonnes (N). The total amount of contained nitrogen contained is released into the atmosphere in an explosion. Most of it will be released in the form of N_2 , but an important part will be released as nitrogen oxide and nitrous oxide.

There is no simple solution. Ammonia demand will continue to rise and technology may or may not bring new solutions. Today's technologies are not "clean" enough to prevent dangerous emission levels. What's more, there are no current alternative technologies to substitute N-fertilizers in the agricultural industry, or N-compounds used in explosives. Additional research and a stricter legislation might be the only choices for the moment.

Figure 12. U.S. Nitrogen Consumption in 1996



Appendix I. U.S. Nitrogen Consumption in 1996
(Thousand metric tonnes of contained nitrogen)

Compound	Production	Imports	Exports	Apparent Consumption
Ammonia	13,200	3,390	435	15,865
Ammonium phosphates	2,821	258	1,596	1,428
Nitric acid	1,855	0	0	1,855
Ammonium nitrate	2,780	271	21	3,030
Explosives	557	0	0	557
Nitrobenzene	78	0	0	78
Aniline-A	76	10	0	86
Toluene diisocyanate	65	0	0	65
Dinitrotoluene	82	0	0	82
Isocyanates	121	0	0	121
Adipic acid (871 tonnes)	0	0	0	0
Urea	3,550	1,170	675	4,045
Melamine	79	0	25	54
Aqueous ammonia	69	0	0	69
Caprolactam	86	0	0	86
Hydrogen Cyanide	319	0	0	319
MMA (653 tonnes)	0	0	0	0
Acrylonitrile	403	0	247	156
Adiponitrile	193	0	0	193
Ammonium sulfate	512	79	222	369
Hexamethylenediamine	Max. 193	0	0	Max. 193

Appendix II. U.S. Nitrogen Wastes and Emissions in 1996

(Thousand metric tonnes of contained nitrogen)

Chemical	N-input (Including Imports)	N-Output (Including Exports)	Process Wastes & Emissions (N)	Other Wastes & Losses	Untreated Emissions (TRI)
Ammonia	16,300	16,300	NA	217	74
Nitric acid	1,935	1,855	80*	-	2.2
Urea	4,720	4,599	NA	121	NA
Melamine	79	79	NA	-	NA
Aqueous ammonia	105	69	36	-	NA
Ammonium sulphate	591	591	NA	-	NA
Ammonium nitrate	3,051	3,051	0.52	-	0.52
Ammonium phosphate	3,079	3,078	0.972	-	0.972
Aniline	86.46	86	0.5	-	0.1
Adipic acid	184	0	185**	-	NA
Hydrogen cyanide (HCN)	323	319	NA	20	0.394
Acrylonitrile (ACN)	413	403	5	-	0.916
Acetonitrile	5.3	5.3	5	-	5
Adiponitrile (ADN)	198	193	4	0.041	0.041
Caprolactam	86	86	NA	-	NA
MMA	94	0	0	0	0
HMDA	193	193	NA	-	NA
Nitrobenzene	85	78	7	-	0.036
Dinitrotoluene	94	82	12	-	0.6
Toluene diisocyanate (TDI)	82	65	17	-	0.85
Isocyanates	124	121	3	-	NA
		Total	352	358	86
		Total Wastes	710		
Fertilizers	11,314				
Explosives	556				
Plastics and fibers	709				
Pesticides & herbicides	36				
Dyes, rubbers & chemicals	16				
Animal feed	283				
Other	1,478				
Total	14,392				

*Approximately 44,000 tonnes (N) are released as N₂, which is totally inoffensive.

** N₂ is released but the amount cannot be determined.

Appendix III. World Nitrogen Consumption in 1996

In 1996 world consumption for ammonia was 102,000,000 tonnes (N) and world trade was 11,400,000 tonnes. According to SRI, 90% of ammonia in the world is ultimately consumed as a fertilizer. Trade for other ammonia sub-products is also very important. About 45% of world production of ammonium phosphates is traded, as well as 18% of ammonium nitrate and 39% of ammonium sulphate. On the other hand, world trade for nitric acid is minimal.

Table 13. World Consumption of Salient Nitrogen Compounds in 1996

Compound	MMT	MMTN
Ammonia	120	102
Nitric acid	55	13.33
Ammonium nitrate	46.75	10
Fertilizer	39.74	8.5
Non-fertilizer	7.01	1.5
Aniline	2.08	0.32
Adipic acid	1,814	0
Urea	38.37	17.9

Source: SRI

Table 14. Distribution of World Nitrogen Consumption

Asia/Oceania	59%
North America	15%
West Europe	12%
Latin America	6%
Central & Eastern Europe	3%
Former Soviet Union	3%
Africa	2%

Source: EFMA, 1988/99

Appendix IV. Comparison of Experimental^a vs. Simulated^b Emission Factors for Detonation of Explosives (kg/tonne)

	CO	CO2	CH4	NH3	HCN	C2H2
TNT						
Experimental	398	-	7.2	14	13	61
Simulated	712	-	76	2.6	13	2.56
PETN						
Experimental	149	-	-	-	-	-
Simulated	177	418	-	-	-	-

^a Source: EPA, 1980

^b Simulation software: Aspen Plus™

References

- ChemExpo, "Chemical Profile: Acrylonitrile," Schnell Publishing, July 14, 1997
<http://www.chemexpo.com/news/PROFILE970721.cfm>
- ChemExpo, "Chemical Profile: Adipic Acid," Schnell Publishing, June 15, 1998
<http://www.chemexpo.com/news/PROFILE980615.cfm>
- ChemExpo, "Chemical Profile: Ammonia," Schnell Publishing, November 29, 1999
<http://www.chemexpo.com/news/profile.cfm>
- ChemExpo, "Chemical Profile: Ammonium Phosphates," Schnell Publishing, September 18, 1995
<http://www.chemexpo.com/news/PROFILEEsept18.cfm>
- ChemExpo, "Chemical Profile: Aniline-A," Schnell Publishing, February 8, 1999
<http://www.chemexpo.com/news/PROFILE990208.cfm>
- ChemExpo, "Chemical Profile: Caprolactam," Schnell Publishing, March 2, 1998
<http://www.chemexpo.com/news/Profile980306.cfm>
- ChemExpo, "Chemical Profile: Hydrogen Cyanide," Schnell Publishing, November 23, 1998
<http://www.chemexpo.com/news/PROFILE981123.cfm>
- ChemExpo, "Chemical Profile: Melamine," Schnell Publishing, October 14, 1996
<http://www.chemexpo.com/news/PROFILEoct14.cfm>
- ChemExpo, "Chemical Profile: Methyl Methacrylate," Schnell Publishing, June 28, 1999
<http://www.chemexpo.com/news/PROFILE990628.cfm>
- ChemExpo, "Chemical Profile: Nitrobenzene," Schnell Publishing, February 15, 1999
<http://www.chemexpo.com/news/PROFILE990215.cfm>
- ChemExpo, "Chemical Profile: Toluene Diisocyanate," Schnell Publishing, April 12, 1999
<http://www.chemexpo.com/news/PROFILE990412.cfm>
- ChemExpo, "Chemical Profile: Urea," Schnell Publishing, August 11, 1999
<http://www.chemexpo.com/news/PROFILE970813.cfm>
- FACT Caprolactam
<http://www.caprolactamfact.com/plant.htm>
- IFA DATA BANK (N, P2O5, K2O), Fertilizer Consumption Statistics
<http://www.fertilizer.org>
- European Fertilizer Manufacturers Association; "Industry Statistics: Market Overview 1988/99"
<http://www.efma.org/statistics>
- Kirk-Othmer; "Concise Encyclopedia of Chemical Technology", John Wiley & Sons, Inc., New York, 1985, pgs. 84, 87, 92- 94, 334, 445- 448, 786, 790, 791, 920.
- Kramer, Deborah A., "Explosives", U.S. Geological Survey-Minerals Information, 1997
<http://minerals.usgs.gov/minerals/pubs/commodity/explosives>
- Plambeck, James A.; "Introductory University Chemistry", November 30, 1995
<http://www.chem.ualberta.ca/courses/plambeck/p101/p01263.htm>
- SRI, "Chemical Economics Handbook Abstract: Acrylonitrile"
<http://ceh.sric.sri.com/Public/Reports/607.5000/Abstract.htm>
- SRI, "Chemical Economics Handbook Abstract: Adipic Acid"
<http://ceh.sric.sri.com/Public/Reports/608.5000/Abstract.htm>
- SRI, "Chemical Economics Handbook Abstract: Ammonium Nitrate"

<http://ceh.sric.sri.com/Public/Reports/757.8000/Abstract.htm>

SRI, "Chemical Economics Handbook Abstract: Ammonium Phosphates"
<http://www-cmrc.sri.com/CIN/MayJune96/Article02.html>

SRI, "Chemical Economics Handbook Abstract: Aniline"
<http://ceh.sric.sri.com/Public/Reports/614.5000/Abstract.htm>

SRI, "Chemical Economics Handbook Abstract: Hexamethylenediamine"
<http://www-cmrc.sri.com/CIN/NovemberDecember96/Article06.html>

SRI, "Chemical Economics Handbook Abstract: Nitric Acid"
<http://www.crbrd.sriconsulting.com/CIN/94/jul-aug/article07.html>

SRI, "Chemical Economics Handbook Abstract: Nitrogen Industry Overview," September-October 1995
<http://www.cbrd.sriconsulting.com/CIN/SeptemberOctober95/Article09.html>

SRI, "Chemical Economics Handbook Abstract: Urea"
<http://www.cbrd.sriconsulting.com/CIN/MayJune95/Article10.html>

Leikam, D.F., Penas, E.J. "Phosphorus Sources for Corn Fertilization", National Corn Handbook 13
<http://www.agcom.purdue.edu/AgCom/Pubs/NCH/NCH-13.htm>

United States Environmental Protection Agency, "Pollution Prevention and Toxics, Acrylonitrile Fact Sheet", December 1994
<http://www.epa.gov/opptintr/chemfact/acry-fs.tx>

United States Environmental Protection Agency, "Pollution Prevention and Toxics, Aniline Fact Sheet" December 1994
<http://www.epa.gov/opptintr/chemfact/anali-sd.tx>

United States Environmental Protection Agency "Pollution Prevention and Toxics, Methyl Methacrylate Fact Sheet", December 1994
<http://www.epa.gov/opptintr/chemfact/methy-sd.tx>

United States Environmental Protection Agency, "Pollution Prevention and Toxics, Nitrobenzene Fact Sheet", February 1995
<http://www.epa.gov/opptintr/chemfact/nitro-sd.tx>

Smil, Vaclav; "Global Population and the Nitrogen Cycle" Scientific America, July 1997
<http://www.greenlink.org/miami/nitrogen.htm>

Endnotes

ⁱ Vaclav Smil, "Global Population and the Nitrogen Cycle", Scientific American July, 1997
<http://www.greenlink.org/miami/nitrogen.htm>

ⁱⁱ Columbia University, "Nitrogen Oxides and Nitric Acid," The Columbia Encyclopedia, Fifth Edition, Columbia University Press, 1993
http://www.ch.ic.ac.uk/mim/environmental/html/nitric_text.htm

ⁱⁱⁱ SRI, "Chemical Economics Handbook Abstract: Ammonium Phosphates"
<http://www-cmrc.sri.com/CIN/MayJune96/Article02.html>

^{iv} Kramer, Deborah A., "Nitrogen Fixed Ammonia", U.S. Geological Survey, Mineral Commodity Summaries, January 1999
<http://minerals.usgs.gov/minerals/pubs/commodity/nitrogen>

^v U.S. Bureau of Census, "1997 Manufacturers Profile", pg. 4-4
<http://www.census.gov/econ/www/manumenu.html>

^{vi} Environmental Protection Agency, "Nitrous Oxide Emissions," Inventory of U.S. Greenhouse Gas Emissions, February 10, 1999
<http://www.epa.gov/oppeoeel/globalwarming/inventory/1998-inv/n2o.htm>

^{vii} Idem

viii Idem

ix European Fertilizer Manufacturers Association, "Production of Nitric Acid: Environmental Data," Brussels, 1997

<http://www.efma.org/publications/bat02>

x Spectrum Laboratories: Chemical Fact Sheet-Cas # 98953

<http://www.epa.gov/opptintr/chemfact/nitro-sd.tx>

xi Thiemens, Mark H., Trogler, William C., "Nylon Production: An Unknown Source of Atmospheric Nitrous Oxide"

xii Inventory of U.S. Greenhouse Emissions, Environmental Protection Agency, February 10, 1999

<http://www.epa.gov/oppeoeel/globalwarming/inventory/1998-inv/n2o.htm>

xiii Lowenheim, Frederick A. and Moran, Marguerite K, "Industrial Chemicals" 4th edition, Wiley-Interscience, New York, 1975

xiv IFA DATA BANK (N, P₂O₅, K₂O), Fertilizer Consumption Statistics

<http://www.fertilizer.org>

xv Preliminary Data Search Report for Locating and Estimating Air Emissions from Sources of Cyanamide Compounds, Environmental Protection Agency, 1993

<http://www.epa.gov/ttnchie1/efdocs/cyanide.pdf>

xvi Idem

xvii Idem

xviii More recent data is not available in World Wide Web.

xix Idem