

# Chapter Three

## Ammonia and the Environment

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### General Environmental Information

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The U.S. Public Health Service's Agency for Toxic Substances and Disease Registry (ATSDR) recently published a document which included a thorough assessment of the environment. *Toxicological Profile for Ammonia* (ATSDR 2004) contains excellent information regarding ammonia and its interaction with the environment. It is important to note that ammonia is not considered to be a contributor to ozone depletion, greenhouse effect, or global warming. Consult the *Toxicological Profile for Ammonia* for the references cited in that document as they are not repeated here. Following is an excerpt from ATSDR *Toxicological Profile for Ammonia* (2004):

#### Overview

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Ammonia is a naturally-occurring compound that is an intermediate in the global nitrogen cycle. It is essential for many biological processes and is a central compound in all living organisms. Nitrogen is converted from atmospheric  $N_2$  to other forms by different processes. Nitrogen fixation (the process of converting atmospheric  $N_2$  to  $NH_3$ ) occurs naturally due to biological processes. Lightning strikes also "fix" atmospheric nitrogen, but they produce nitrogen oxides, not ammonia. The current amount of nitrogen fixation that occurs by industrial processes equals that of natural, terrestrial nitrogen fixation. Both natural and anthropogenic sources produce a total of approximately 230–270 million metric tons of  $NH_3$  per year.

Because of its role in natural processes and cycles, ammonia is found at low concentrations in most environmental media. When ammonia is found at a local concentration that is higher than these background levels, it is often a result of human influence. Ammonia is hazardous only when exposure is to high levels. In determining the environmental fate of ammonia, several factors should be considered, the primary one being that ammonia is the most abundant alkaline gas in the environment. An acid-base reaction between water and ammonia occurs such that the dominant form of ammonia in water, at environmentally relevant pHs, is the ammonium ion. In media where water is usually present, such as soil, plants, biological tissue, and water itself, ammonia and ammonium are in dynamic equilibrium.

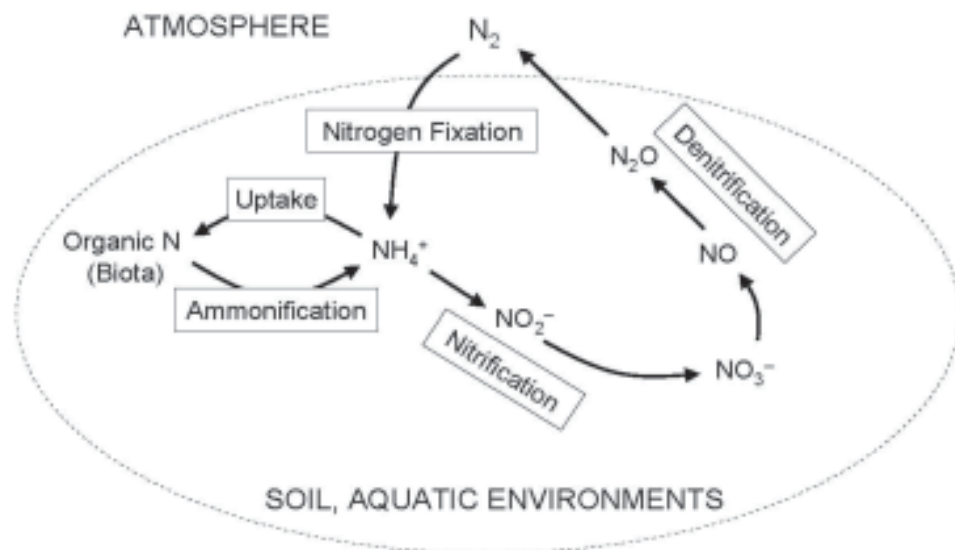
Ammonia is a key intermediate in the nitrogen cycle, a natural cycle that is coupled with other important biological cycles (i.e., the sulfur cycle and carbon cycle). An understanding of the role of ammonia in the nitrogen cycle, at least on a generalized level, is important in determining the environmental fate of ammonia. A simplified schematic of the microbial processes of the nitrogen cycle that involves ammonia can be found in Figure 3-1. Microorganisms perform four processes in the nitrogen

cycle that result in production or transformation of ammonia: nitrogen fixation, nitrification, denitrification, and ammonification. As part of this cycle, nitrogen gas and oxidized forms of nitrogen are transformed and returned to the biological world. Nitrogen fixation is the process whereby atmospheric nitrogen gas is converted to ammonia, which is then assimilated into amino acids; it has been found that there is only a small proportion of all genera of microorganisms that can fix nitrogen. Denitrification is the process whereby the nitrogen oxides (i.e., nitrate and nitrite) are reduced under anaerobic conditions to  $N_2$  and  $N_2O$ , which can escape to the atmosphere. Nitrification is the biological oxidation of ammoniacal nitrogen to nitrate, with nitrite as the intermediate. Ammonification (or nitrogen mineralization) is the conversion of organic nitrogen into ammonia.

Ammonia may be released to the atmosphere by volatilization from the following sources: decaying organic matter; livestock excreta; fertilizers applied to soils; venting of gas, leaks, or spills during commercial synthesis, production, transportation, or refrigeration equipment failure; sewage or waste water effluent; burning of coal, wood, and other natural products; and volcanic eruptions.

Ammonia may be released to water through effluent from sewage treatment plants, effluent from industrial processes, runoff from fertilized fields, and runoff from areas of concentrated livestock. This usually occurs when organic N compounds present in these sources enter the water and are converted microbiologically to ammonia.

FIGURE 3-1. Simplified Schematic for the Microbial Processes of the Nitrogen Cycle (ATSDR 2004).



Ammonia may be released to soils by natural or synthetic fertilizer application, animal (including livestock) excrement degradation, decay of organic material from dead plants and animals, and indirectly from natural fixation of atmospheric nitrogen. In this latter case, ammonia releases can occur following nitrogen fixation by free-living microbes and plants (those that are symbiotic nitrogen-fixing bacteria), which subsequently die and release ammonia livestock. This usually occurs when the organic N compounds present in these sources enter the water and are converted microbiologically to ammonia (or compounds that are converted to ammonia) to the soils.

In the atmosphere, ammonia can be removed by rain or snow washout. Reactions with acidic substances, such as  $H_2SO_4$ ,  $HCl$ ,  $HNO_3$ , or  $N$  oxides (all produced in high concentrations from anthropogenic activities) produce ammonium aerosols, which can undergo dry or wet deposition. The gas phase reaction of ammonia with photochemically produced hydroxyl radicals is thought to contribute about 10% to the overall atmospheric removal process. The best estimate of the half-life of atmospheric ammonia is a few days.

In water, ammonia volatilizes to the atmosphere, is transformed to other nitrogenous compounds, or may be bound to materials in the water. Volatilization is highly pH-dependent, and can also depend on other factors such as temperature, wind speed, and atmospheric ammonia concentration. Transformation of ammonia in water occurs primarily by the microbial processes of nitrification and to lesser extents, denitrification. Nitrification yields nitrate and nitrite anions; the former species can be responsible for methemoglobinemia in human infants if the contaminated water is ingested. Removal of ammonium from water can also occur by adsorption to sediments or suspended organic material.

In soil, ammonia may either volatilize to the atmosphere, adsorb to particulate matter, or undergo microbial transformation to nitrate or nitrite anions. Uptake by plants can also be a significant fate process. Ammonia at natural concentrations in soil is not believed to have a very long half-life. If ammonia is distributed to soil in large concentrations (e.g., following an application of an ammonia-containing fertilizer), the natural biological transformation processes can be overwhelmed, and the environmental fate of ammonia will become dependent upon the physical and chemical properties of ammonia, until the ammonia concentration returns to background levels.

Occupational exposure to ammonia may occur in industries involved in its synthesis, formulation, processing, transportation, and use. Occupational exposure to ammonia can also occur during the use of an extensive number of cleaning products that contain ammonia. Farmers may be exposed during the application of fertilizers containing anhydrous ammonia or liquid ammonia, or manures high in ammonia. Workers at cattle feedlots, poultry confinement buildings, or other industries that have a high concentration of animals may also be exposed.

Exposure of the general population to elevated levels of ammonia is most commonly from the use of household cleaners that contain ammonia. People who live near farms or who visit farms during the application of fertilizer that contain or release ammonia may also be exposed. People living near cattle feedlots, poultry confinement buildings, or other areas where animal populations are concentrated can also be exposed to ammonia, in addition to other gases generated by putrefaction. Ammonia has been identified at 137 out of 1,647 NPL hazardous waste sites (HazDat 2004).

## *Releases to the Environment*

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Continuation of excerpt from ATSDR *Toxicological Profile for Ammonia* (2004). Consult the *Toxicological Profile for Ammonia* for the references cited in that document as they are not repeated here.

Ammonia is commercially produced for many processes, but most production is for agricultural uses, primarily crop fertilizer. As a result of most it being formulated for agricultural practices, ammonia is commonly distributed to the environment during its intended use as a crop fertilizer. Release data generated for the Toxics Release Inventory (TRI) (see Table 3-1) provide detailed information regarding environmental releases related to industrial activities, but should be used with caution because only certain types of facilities are required to report, and data from these reports do not represent an exhaustive list of all commercial releases. It should be noted that for ammonia, since it is one of the most widely-used agricultural fertilizer chemicals in the United States, the TRI data represent only a small fraction of the environmental release, and do not include releases that occur during farming or other agriculture practices.

Table 3-1 shows the 2001 TRI releases of ammonia from manufacturing or processing facilities to different environmental compartments. Most of the ammonia released to the environment from these facilities was the result of air releases, followed by releases via underground injection. The greatest air releases occurred in the state of Louisiana (12,304,532 pounds), which was almost 2 million more pounds released than the second highest releasing state, Ohio (10,505,480 pounds). Texas released the most ammonia via underground injection (15,014,490 pounds), which was more than 3 times the second highest releasing state, Louisiana (4,446,211 pounds). For all on-site releases, the two states releasing the most ammonia were the adjacent states of Louisiana and Texas (Louisiana released 17,742,736 pounds and Texas released 21,354,611 pounds).

Release of ammonia from production and processing facilities has changed from year to year, with amounts generally decreasing since the early 1990s. Reported air releases have ranged from a high of 254,542,289 pounds in 1989 to a low of 122,057,546 pounds in 2001. Surface water releases have ranged from a high of 48,138,279 pounds in 1990 to a low of 6,621,166 pounds in 2001. Land releases (surface releases) have shown a similar trend, with the highest amount (17,782,641 pounds) released in 1990, and the lowest amount (2,868,728 pounds) released in 1999. The general trend is that less and less ammonia has been released to the environment each year, such that the total amount released in 2001 (158,521,046 pounds) was less than a third of the amount released in 1990 (548,828,735 pounds).

The TRI data should be used with caution because only certain types of facilities are required to report. This is not an exhaustive list.

In addition to releases related to agricultural or other anthropogenic usage, ammonia has been identified in several environmental compartments including surface water, groundwater, soil, and sediment collected at 135 of the 1,647 current or former NPL hazardous waste sites in the United States, and in groundwater and soil samples at 2 sites in Puerto Rico (HazDat 2004). Furthermore, ammonia is a key intermediate in nature's nitrogen cycle, and considerable amounts are released to the environment as a result of natural processes. As a result of inputs from natural sources and from anthropogenic sources, ammonia concentrations in nature are in dynamic equilibrium. When ammonia is found at elevated concentrations, however, it is usually a result of anthropogenic activity.

**TABLE 3-1 Releases to the Environment from Facilities that Produce, Process, or Use Ammonia<sup>a</sup>**

State <sup>c</sup>	No. of facilities	Reported amounts released in pounds per year <sup>b</sup>						
		Air <sup>d</sup>	Water	Under-ground injection	Land	Total on-site release <sup>e</sup>	Total off-site release <sup>f</sup>	Total on and off-site release
AK	7	1,427,011	32,428	5	95,950	1,555,394	0	1,555,394
AL	75	3,192,615	180,703	0	57,288	3,430,606	145,305	3,575,911
AR	48	3,672,621	209,122	0	372	3,882,115	18,078	3,900,193
AS	1	6,920	No data	0	0	6,920	0	6,920
AZ	18	107,967	5	0	260	108,232	350	108,582
CA	178	6,362,240	37,470	41,236	264,004	6,704,950	18,728	6,723,678
CO	19	291,922	12,899	0	4,019	308,840	148	308,988
CT	28	169,071	10,035	0	0	179,106	8	179,114
DC	2	0	487	0	0	487	0	487
DE	14	109,356	3,804	0	7,937	121,097	0	121,097
FL	72	5,646,496	148,226	293,106	124,914	6,212,742	122,755	6,335,497
GA	95	8,291,371	171,670	0	13,140	8,476,181	154,582	8,630,763
HI	7	47,492	660	2,059	30,368	80,579	0	80,579
IA	60	4,686,900	133,403	0	3,829	4,824,132	166,223	4,990,355
ID	16	2,705,639	5,874	0	182,369	2,893,882	21,731	2,915,613
IL	136	2,366,356	56,440	0	68,423	2,491,219	1,108,621	3,599,840
IN	82	1,294,431	55,681	824,984	61,545	2,236,641	23,002	2,259,643
KS	38	3,285,064	36,461	22,555	270,459	3,614,539	42,129	3,656,668
KY	40	1,218,869	83,020	0	4,000	1,305,889	1,483	1,307,372
LA	78	12,304,532	917,883	4,446,211	4,816	17,673,442	69,294	17,742,736
MA	48	591,589	6	0	0	591,595	33,235	624,830
MD	17	482,934	25,246	0	18,569	526,749	4,587	531,336
ME	15	813,198	39,047	0	0	852,245	0	852,245
MI	81	1,579,680	141,346	40,307	68,851	1,830,184	12,981	1,843,165
MN	56	1,790,288	43,283	0	36,315	1,869,886	3,315	1,873,201
MO	55	548,485	319,685	0	11,624	879,794	34,796	914,590
MS	49	4,452,540	394,837	0	46,552	4,893,929	255	4,894,184
MT	14	543,332	10,920	0	9,685	563,937	0	563,937
NC	101	3,054,435	287,555	0	30,750	3,372,740	18,711	3,391,451
ND	9	305,283	17,106	0	88,654	411,043	340	411,383
NE	38	804,872	245,587	0	377,539	1,427,998	243,327	1,671,325
NH	15	128,420	551	0	0	128,971	966	129,937
NJ	67	1,144,702	165,642	0	0	1,310,344	18,406	1,328,750
NM	5	9,780	5	29,497	670	39,952	0	39,952
NV	13	428,880	2,710	0	311,810	743,400	0	743,400
NY	71	1,387,982	61,780	0	8,266	1,458,028	1,540	1,459,568
OH	136	10,505,480	98,996	2,006,500	52,964	12,663,940	93,861	12,757,801
OK	28	5,995,915	81,112	0	25,716	6,102,743	1,850	6,104,593
OR	51	1,769,989	43,747	0	106,233	1,919,969	1,882	1,921,851
PA	131	2,346,403	229,268	0	13,469	2,589,140	23,359	2,612,499
PR	16	1,938,727	306	0	0	1,939,033	600	1,939,633
RI	22	84,982	3,573	0	0	88,555	0	88,555
SC	68	2,559,694	162,782	0	39,741	2,762,217	5,627	2,767,844
SD	9	86,361	684	0	225	87,270	29,223	116,493
TN	58	4,865,087	487,650	0	796	5,353,533	78,192	5,431,725
TX	209	5,206,675	518,396	15,014,390	199,710	20,939,171	415,440	21,354,611
UT	29	458,197	8,800	0	911,305	1,378,302	503	1,378,805
VA	64	7,866,819	93,001	0	35,707	7,995,527	129,614	8,125,141
VI	1	77,675	42,154	0	119,829	0	0	119,829
VT	2	47,582	4,450	0	0	52,032	0	52,032
WA	45	857,165	137,956	0	22,488	1,017,609	80,200	1,097,809
WI	83	589,027	89,624	0	3,107	681,758	78,850	760,608
WV	36	961,276	758,661	14,387	0	1,734,324	42,951	1,777,275
WY	12	587,219	8,429	239,000	6,610	841,258	0	841,258
<b>Total</b>	<b>2,668</b>	<b>122,057,546</b>	<b>6,621,166</b>	<b>22,974,237</b>	<b>3,621,049</b>	<b>155,273,998</b>	<b>3,247,048</b>	<b>158,521,046</b>

Source: TRI01 2003 (Data are from 2001)

<sup>a</sup>The TRI data should be used with caution since only certain types of facilities are required to report. This is not an exhaustive list. Data are rounded to nearest whole number.

<sup>b</sup>Data in TRI are maximum amounts released by each facility.

<sup>c</sup>Post office state abbreviations are used.

<sup>d</sup>The sum of fugitive and stack releases are included in releases to air by a given facility.

<sup>e</sup>The sum of all releases of the chemical to air, land, water, and underground injection wells.

<sup>f</sup>Total amount of chemical transferred off-site, including to publicly owned treatment works (POTW).

### **Air**

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Large amounts of ammonia are released to the atmosphere worldwide by domesticated farm animals (ApSimon et al. 1987; Asman and Janssen 1987; Buijsman et al. 1987; Kramer 2000, 2002; Ryden et al. 1987). Ammonia emissions due to the decay of livestock manure are a source for ammonia release in areas that have artificially high concentrations of animals, such as cattle feedlots and poultry-confinement buildings (Brinson et al. 1994; Hutchinson et al. 1982; Langland 1992; Liao and Bundy 1995; Olivier et al. 1998; Sunesson et al. 2001). In Germany, over 90% of the measured NH<sub>3</sub> emissions originated from agricultural sources (Strogies and Kallweit 1996). In Russia, estimated NH<sub>3</sub> emissions from fertilizer applications and livestock sources accounted for 94% of the total NH<sub>3</sub> emissions from all anthropogenic sources (Tsibulski et al. 1996). The use of high nitrogen content feed for farm animals and the trend toward larger feedlots have been responsible for increased emissions in developed countries.

The application of fertilizer to soil, as ammonia, ammonium compounds, or ammonia precursors (such as urea), is a well documented source of ammonia release to the atmosphere (ApSimon et al. 1987; Beyrouthy et al. 1988; Buijsman et al. 1987; Kucey 1988; Olivier et al. 1998; Reynolds and Wolf 1988). The rate of ammonia emission from ground sources, such as freshly fertilized fields and cattle feedlots, is dependent on variables such as the pH, temperature, soil characteristics, rainfall, method of application, wind speed, etc. (Bouwmeester and Vlek 1981; Brunke et al. 1988; Denmead et al. 1982; Hoff et al. 1981; Kucey 1988; Nason et al. 1988; Reynolds and Wolf 1988). Ammonia can volatilize from sewage sludge that has been spread on the surface of the soil (Beauchamp et al. 1978; Ryan and Keeney 1975) as well as from poultry litter (Brinson et al. 1994). In the latter case, composted poultry litter released far less volatile NH<sub>3</sub> to the atmosphere (0–0.24% of applied) than did fresh poultry litter (17–23%) (Brinson et al. 1994). In contrast, the crops themselves are often minor sources of atmospheric NH<sub>3</sub>. Harper and Sharpe (1995) demonstrated almost no net atmospheric NH<sub>3</sub> flux in corn crops, due to their relatively similar emission and uptake rates of NH<sub>3</sub> over the growing season.

For much of the history of the Earth, biological activity in soil and natural waters was the primary global source of atmospheric ammonia (Dawson 1977; Dawson and Farmer 1984; National Science Foundation 1999), but this has changed over the last century. Crutzen (1983) suggested that the decay of organic material arising

from dead plant, animal, and microbial biomass generates most of the atmospheric ammonia, while Galbally (1985) and Irwin and Williams (1988) suggested that domestic-animal excretions represent the dominant source of atmospheric ammonia. Lee et al. (1997) estimated that grasslands contributed 40% of the total global  $\text{NH}_3$  emissions, with domestic animal wastes contributing 42.3% of that. Recent studies, however, provided fairly uniform estimates of ~40% of global  $\text{NH}_3$  emissions being due to excreta from domestic animals (Asman et al. 1998; Bouwman et al. 1997; Olivier et al. 1998). Current measurements and estimates, however, indicate that the amount of ammonia produced as a result of anthropogenic activities is equivalent to the amount produced by natural processes (National Science Foundation 1999).

In addition to livestock-related releases, ammonia can be released to the atmosphere through the venting of gases during the production, storage, and transportation of ammonia, and during its formulation or incorporation into secondary products (Buijsman et al. 1987). Long pipelines are used to transport ammonia from its site of manufacture to agricultural areas where it is used as fertilizer (Farm Chemicals Handbook 1987; Kramer 2000; LeBlanc et al. 1978). Releases to the atmosphere could occur at pumping stations and points of transfer along these pipelines, or from leaks. Large refrigerated tanks are used to store ammonia, and release to the environment can occur while venting the pressure in these tanks, or from leaks.

Ammonia can also enter the atmosphere by volatilization from the waste water of industrial processes that involve its production or use, and from the volatilization from the effluent of waste water treatment plants (Buijsman et al. 1987; Langland 1992; Roy and Poricha 1982; Wilkin and Flemal 1980). Ammonia has been found in the exhaust of automobile and diesel engines (Asman et al. 1998; Plerson and Brachaczek 1983). Release to the atmosphere can occur during the burning of coal (Bauer and Andren 1985; Olivier et al. 1998). The latter process, however, is not thought to account for a significant proportion of the total anthropogenic ammonia released to the atmosphere (Olivier et al. 1998; Strogies and Kallweit 1996).

Natural sources of ammonia emissions to the atmosphere are volcanic eruptions, forest fires, and the decomposition of nitrogenous compounds arising from microbially-fixed nitrogen (Galbally 1985; Hegg et al. 1987; National Science Foundation 1999). Excreta from household pets, wild animals, and humans are also contributing sources (Asman and Drukker 1988; Buijsman et al. 1987; Crutzen 1983).

## Water

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The major point source of release to surface waters is from the effluents of waste water-treatment plants (Barica 1990; Crumpton and Isenhardt 1988; Wilkin and Flemal 1980). Ammonia can enter surface waters through the effluent of commercial processes in which ammonia is used or produced (Effler et al. 2001; Huddleston et al. 2000; Matthews et al. 2000; Roy and Poricha 1982). Runoff from fertilized farmland and from areas of concentrated livestock production can also result in the transfer of ammonia to surface water (Corsi et al. 2000; Jingsheng et al. 2000; Wilkin and Flemal 1980). Surface water can absorb ammonia directly from the atmosphere near cattle feedlots, areas where the local atmospheric concentration may be high (Fangmeier et al. 1994; Hutchinson and Viets 1969). Ammonium can also be released to water when  $\text{N}_2$ -fixing cyanobacteria (also called blue-green algae) die and are decomposed.

## Soil

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Ammonia enters soil through different processes, primarily human practices (e.g., fertilizer applications, animal husbandry), and natural biological processes. Direct application of fertilizers represents a major influx of ammonia into soils. Of the total U.S. production of anhydrous ammonia, 30% is applied directly to the soil under pressure (Kramer 2000). Approximately 80% of the U.S. production of ammonia is applied to soil in fertilizer formulations designed to release ammoniacal nitrogen. Application of natural fertilizers obtained from livestock excreta will also result in the release of ammonia to the soil (Asman et al. 1998; Beauchamp et al. 1982; Hoff et al. 1981; Olivier et al. 1998). High levels of ammonia in soils can result from the decomposition of animal wastes on cattle feedlots or other confinement areas, as well as from the land disposal of livestock and poultry waste. Ammonia in soil can also arise from the decay of organic material arising from plant, animal, and microbial byproducts and biomass (Dawson 1977; Dawson and Farmer 1984). Microbial fixation of nitrogen from the atmosphere is a natural and continual source of ammonia in soil, which can be released to soil after the microorganisms die (Galbally 1985; National Science Foundation 1999).

In nature, there are many pathways for incorporation of ammonia into soil. Natural sources include microbial decomposition of dead plants and animals, and hydrolysis or breakdown of urea and nitrogenous waste products in animal excretions. Several species of microorganisms can produce ammonia by the fixation of  $N_2$ , and these organisms are widely dispersed throughout the soil (Atlas and Bartha 1998; Crutzen 1983); ammonia is released to the soil only after these microorganisms die. While several species of microbes can perform nitrogen fixation, this capability would not be one that is considered common for most microorganisms.

## Environmental Fate

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In considering the environmental fate of ammonia, it is necessary to emphasize that ammonia is very important in nature and in nature's biological cycles. In our limited understanding of fluxes between these cycles, ammonia is considered a key intermediate. Nature has incorporated many mechanisms and "rules" for altering the distribution of ammonia through the biological system, as circumstances dictate. An in-depth discussion of these phenomena is outside the scope of this document; however, it is important to understand that for ammonia, all organisms contribute, either directly or indirectly, to the direction and distribution of the various environmental-fate processes.

An important consideration that affects the transport and partitioning of ammonia in the environment is that ammonia is a base. As a base, the physical and chemical properties of ammonia are pH-dependent, and thus, environmental-fate processes that influence the transport and partitioning of  $NH_3$  will also be pH-dependent. For some environmental fate processes, a change in pH may only affect the relative rate of a process, while for others, it could change the direction or overall result of that process. The influence of pH on the environmental fate of ammonia will be discussed where appropriate. Temperature is also an important consideration in the environmental fate of ammonia. Temperature, although to a lesser extent than pH, affects the ammonia-ammonium equilibrium.



## Transport and Partitioning

Atmospheric ammonia can be readily removed from the air by rain or snow washout (Adamowicz 1979; Asman et al. 1998; Kumar 1985). It can dissolve in the water found in clouds (Asman et al. 1998; Brimblecombe and Dawson 1984; Sprenger and Bachmann 1987) or fog (Johnson et al. 1987). Ammonia can be removed from the atmosphere through the direct absorption by surface waters in areas where the local atmospheric concentration is high (Hutchinson and Viets 1969) and by wet deposition onto soils and surface waters (Asman et al. 1998; Cuesta-Santos et al. 1998; Goulding et al. 1998). Uptake of atmospheric ammonia by different species of plants also occurs (Harper and Sharpe 1995; Nason et al. 1988; Rogers and Aneja 1980). Depending on the local atmospheric concentration, however, plants can also release ammonia to the atmosphere (Harper and Sharpe 1995; Lee et al. 1997; O'Deen and Porter 1986; Parton et al. 1988). By use of  $^{15}\text{NH}_3$ , it has been demonstrated that minerals and dry soil can rapidly and effectively adsorb  $\text{NH}_3$  from air containing trace quantities of this gas (Bremner 1965). Ammonia is the predominant basic gas in the atmosphere (Allen et al. 1989). As such, it is capable of rapidly reacting with atmospheric  $\text{H}_2\text{SO}_4$ ,  $\text{HNO}_3$ , or  $\text{HCl}$ , forming ammonium aerosols, which can then undergo dry deposition (Allen et al. 1989; Irwin and Williams 1988).

If released to surface water, ammonia can volatilize to the atmosphere or be taken up by aquatic plants. The rate of volatilization of ammonia from water will increase with increasing pH (generally only important above pH values of  $\sim 7.0$ ) and temperature, and can be influenced by other environmental factors. Gaseous or liquid ammonia added to water will increase the pH of the medium; the rate of volatilization may increase dramatically if large amounts are released to relatively small static bodies of water, such as rice paddies (DeDatta 1995). Agitation will also increase the rate of volatilization. Georgii and Gravenhorst (1977) calculated the equilibrium concentration of ammonia above the Pacific Ocean. Using a constant concentration of 3 pmol/L, the ammonia concentration above the ocean as a result of increased volatilization was calculated to change from approximately 2.8 to 7 ppb as the pH was increased from 8.1 to 8.4 (at 25°C). Volatilization of ammonia from flooded rice paddies was found to increase with increasing ammoniacal nitrogen concentration, pH, temperature, and wind velocity (Bouwmeester and Vlek 1981; DeDatta 1995; Tian et al. 2001). Ammonia can also be taken up by aquatic plants as a source of nutrients (Kemp and Dodds 2002).

In water, adsorption of ammonia to sediment and suspended organic material can be important under proper conditions (Ankley et al. 1990). Adsorption to sediment should increase with increasing organic content, increased metal ion content, and decreasing pH. Ammonia, however, can be produced in, and subsequently released from, sediment (Jones et al. 1982; Malcolm et al. 1986).

The uptake of ammonia by fish can also occur under the proper conditions (Hargreaves 1998; Mitz and Giesy 1985). Ammonia is the final breakdown product of nitrogenous-compound metabolism for catfish, and it is normally released through the gills into the surrounding water, driven by a concentration gradient. If the water concentration is abnormally high, the direction of passive ammonia transport is reversed.

A complete discussion of the factors influencing the transport and partitioning of ammonia in soil is outside the scope of this document. Adsorption of ammonia occurs in most moist or dry soils, and ammonia is predominantly, but not exclusively,

held as the ammonium ion. Generally, adsorption will increase with increasing organic-matter content of the soil, and will decrease with increasing pH. Other factors that influence the adsorption of ammonia to soil are the presence of metallic ions, the predominant microbial populations and communities present, and its rate of uptake by plants. The ammonia concentration, temperature, and wind speed can also subtly affect the adsorption process by influencing the rate of volatilization (Bouwman et al. 1997; Bouwmeester and Vlek 1981; Brunke et al. 1988; Denmead et al. 1982; Galbally 1985; Goulding et al. 1998; Hoff et al. 1981; Kucey 1988; Nason et al. 1988; Reynolds and Wolf 1988; Socolow 1999). To demonstrate the influence of pH on the volatilization of ammonia (which, as indicated above, influences the potential for ammonia adsorption), ammonia loss was measured in greenhouse experiments using soils that had been adjusted to different pH values. Following the application of manure to the soil surface, ammonia volatilization was found to be 14% of the applied ammonium at a soil pH of 6.4 (manure pH=6.4). At a soil pH of 7.0 (manure pH=7.8), 65% was lost by volatilization (Hoff et al. 1981). In a study of the effects of SO<sub>2</sub> deposition on soils, it was found that the threshold pH at which ammonia volatilization from soil was drastically reduced did not occur until the pH was reduced to between pH 3.5 and 4.0 (Mahendrappa 1982). This is a relatively unrealistic and unrepresentative pH value for most soils; the results, however, indicate that volatilization will be an important process that affects the transport and partitioning of ammonia in most soils.

Because ammonia, as ammonium ion, is the nutrient of choice for many plants (Kramer 2000; Rosswall 1981), uptake of soil ammonia by living plants is an important fate process. The rate of uptake by plants varies with the growing season. At normal environmental concentrations, ammonia does not have a very long residence time in soil. It is either rapidly taken up by plants, bioconverted by the microbial population, or volatilized to the atmosphere. Because of these processes, and because ammonia generally exists in soils as NH<sub>4</sub><sup>+</sup> (which binds to soils particles), ammonia does not leach readily through soil; thus, it is rarely found as a contaminant of groundwater (Barry et al. 1993). In soil, ammonia that results from the application of fertilizers is usually found in the top 10 inches of the soil (Beauchamp et al. 1982). However, nitrate derived from ammonia may leach to groundwater.

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## Transformation and Degradation

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### Air

In air, a dominant fate process for ammonia is the reaction with acid air pollutants. Formation of particulate NH<sub>4</sub><sup>+</sup> compounds by reactions with HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> is rapid (Bouwman et al. 1997; Irwin and Williams 1988). The extent to which this process serves as a removal mechanism depends on the concentrations of these acidic compounds (Goulding et al. 1998). Thus, it is likely more important in areas of high industrial activity or a high density of automobile traffic, but of lesser importance over rural areas. These ammonium compounds can then be removed by dry or wet deposition.

The vapor-phase reaction of ammonia with photochemically produced hydroxyl radicals is known to occur. The rate constants for this reaction have been determined to be 1.6x10<sup>-13</sup> cm<sup>3</sup>/molecule-sec, which translates to a calculated half-life of 100 days at a hydroxyl radical concentration of 5x10<sup>5</sup> molecules/cm<sup>3</sup> (Graedel 1978). This process reportedly removes 10% of atmospheric ammonia (Crutzen 1983).

Since ammonia is very soluble in water, rain washout is expected to be a dominant fate process. The half-life for ammonia in the atmosphere was estimated to be a few days (Brimblecombe and Dawson 1984; Crutzen 1983; Dawson 1977; Galbally and Roy 1983; Moller and Schieferdecker 1985). The reaction of atmospheric ammonia with acidic substances in the air results in the formation of ammonium aerosols that can subsequently be removed from the atmosphere by dry or wet deposition. In general, dry deposition processes predominate where there are high amounts of  $\text{NH}_3$  emissions; where  $\text{NH}_3$  emissions are lower, wet deposition of particulate  $\text{NH}_4^+$  predominates (Asman et al. 1998).

### Water

In surface water, groundwater, or sediment, ammonia can undergo sequential transformation by two processes in the nitrogen cycle, nitrification and denitrification, which would produce ionic nitrogen compounds, and from these, elemental nitrogen. The ionic nitrogen compounds formed from the aerobic process of nitrification,  $\text{NO}_2^-$  and  $\text{NO}_3^-$ , can leach through the sediment or be taken up by aquatic plants or other organisms. High concentrations of nitrate in groundwater can cause methemoglobinemia in infants when contaminated water is ingested (Messinga et al. 2003, Payne 1981). Elemental nitrogen formed from the anaerobic process of denitrification is lost by volatilization to the atmosphere.

In water, ammonia is in equilibrium with the ammonium ion,  $\text{NH}_4^+$ . The ammonia-ammonium ion equilibrium is highly dependent on the pH and, to a lesser extent, the temperature of the medium. In acidic waters and neutral waters, the equilibrium favors the ammonium ion.

### Sediment and Soil

In soil, ammonia can serve as a nutrient source for plants, which can be taken up by plants and microorganisms and converted to organic-nitrogen compounds. Ammonia in soil can be rapidly transformed to nitrate by the microbial population through nitrification (Atlas and Bartha 1998; Payne 1981). The nitrate formed will either leach through the soil or be taken up by plants or other microorganisms. Very high localized concentrations of ammonia, such as those that might occur after a spill, or an excessive application, of ammonia-containing fertilizers can be toxic to plants, other organisms, or microbiota, which if inhibited or killed, will result in a decrease of the rates of any related nitrogen transformation processes. Under these conditions, other fate processes dictated by the physical and chemical properties of ammonia will dominate until the ammonia concentration returns to a background level. These physical and chemical processes include binding to soil particles (including organic carbon) or undergoing volatilization to the atmosphere.

### Other Environmental Media

The ammonia concentrations measured in the plumes of seven forest fires in the western United States ranged from 7 to 130 ppb; the median value of the 13 measurements was 37 ppb (Hegg et al. 1987, 1988). Fangmeier et al. (1994) reported a slightly higher value for smoke from a forest fire in Canada, 250 ppb. Ammonia has been found in the exhaust of automobile and diesel engines (Plerson and Brachaczek 1983). Ammonia has also been determined to be a component of tobacco and cigarette smoke (Sloan and Morie 1974).

### **Bioavailability from Environmental Media**

The bioavailability of ammonia from air and water has been examined rather extensively in animals. Bioavailability from soil has not been studied, although it is not a likely source of exposure.

### **Food Chain Bioaccumulation**

Ammonia is a naturally-occurring compound and a key intermediate in the nitrogen cycle. Since it is continually recycled in the environment, bioaccumulation, as it is usually considered, does not occur. Thus, data on this process are not warranted.

### **Exposure Levels in Environmental Media**

As an intermediate in the nitrogen cycle, ammonia is naturally present in environmental media. Measurements of ammonia in environmental media are sufficient to distinguish between background concentrations and elevated concentrations. Data regarding ammonia levels in soil samples, however, appear not to be as complete as the database for air and water.

Determining low level concentrations of atmospheric ammonia in the presence of ammonium salts is difficult. Recently, investigators have been establishing new methods for the analysis of ammonia in the presence of ammonium compounds (see Chapter 7, ATSDR Toxicological Profile for Ammonia 2004). If highly accurate values for low levels of ammonia are necessary, then a re-evaluation of older literature values might be necessary.

### **Exposure Levels in Humans**

Data regarding the exposure levels of ammonia are sufficient for understanding the sources and approximate magnitudes of human exposure. Quantitative monitoring data for specific circumstances, occupations, or events, as reported in the current literature, might be considered to be lacking. Monitoring data for ammonia concentrations in the average household are generally adequate. Reports indicate that while background indoor concentrations of chemicals such as ammonia are sometimes higher inside than outside the home, the levels of exposure do not generally have effects on residents. This exposure, however, would be expected to be higher when ammonia-containing cleaning products are used, or when other ammonia-containing compounds are used in the household, and effects under these conditions would depend on the exposure concentration and duration.

### **Exposures of Children**

Data regarding the exposure levels of ammonia to children were not extensive enough for evaluating the sources and approximate exposures to children. As was found with data in the section for Exposure Levels in Humans above, quantitative monitoring data might be considered lacking. A few recent studies indicate that exposures to, and effects of, ammonia on children are generally minimal, and do not influence the respiratory health of the children studied. However, more studies could be conducted to verify these findings. Child health data needs relating to susceptibility are discussed in Section 3.12.2 Identification of Data Needs: Children's Susceptibility.

### Exposure Registries

No exposure registries for ammonia were located. This compound is not currently one of the compounds for which a subregistry has been established in the National Exposure Registry (Agency for Toxic Substances and Disease Registry 1999). The compound will be considered in the future when chemical selection is made for subregistries to be established. The information that is amassed in the National Exposure Registry facilitates the epidemiological research needed to assess adverse health outcomes that may be related to exposure to this compound.

### Ongoing Studies

The Federal Research in Progress (FEDRIP 2003) database and Current Research Information System (CRIS) database (USDA 2003) provide additional information obtainable from a few ongoing studies that may fill some of the data needs identified in Section 6.8.1. These studies are summarized in Table 3-2. Most of the studies are investigating approaches that reduce exposures to ammonia, emissions of ammonia during agricultural practices, and novel systems to reduce those emissions.

**TABLE 3-2 Ongoing Studies on Environmental Fate and the Potential for Human Exposure to Ammonia**

Investigator	Affiliation	Research and Description	Sponsor
Bazemore RA; Chen TC	Mississippi State University	Evaluation of effectiveness of five substances (copper chlorophyllin complex, chitosan, activated carbon, kenaf, and paper mill sludge) in reducing ammonia emissions from animal waste compost.	Hatch
Harper LA; Sharpe RR	ARS, Athens, Georgia	Investigation of the generation and deposition of ammonia aerosols from swine waste, which is then compared to meteorological fluxes, with the objective being to reduce short-term and long-term ammonia losses that affect the local environment.	USDA in house
Hristov AN	University of Idaho	This proposal seeks, through dietary means, better capture of ruminal ammonia-nitrogen into microbes and consequently into milk. This will increase the efficiency of utilization of feed N and reducing N excretions in the dairy cow.	NRI comp. grant
Walsh JL Jr.	Georgia Institute of Technology	The objective is to develop an integrated-optics (IO) sensor capable of measuring gaseous ammonia concentrations in the range of 100 ppb. This will be used to measure losses from agricultural croplands after application of nitrogen fertilizers.	U. S. DOE
Wilhelm LR et al.	University of Tennessee at Knoxville	Emission data and production information will be gathered from facilities country-wide for poultry and swine buildings. Evaluation of factors related to ammonia emissions will be conducted, and cost-effective approaches for reducing emissions considered and evaluated.	Hatch

Source: CRIS 2003; FEDRIP 2003

ARS = Agricultural Research Service

NRI = National Research Institute

USDA = U.S. Department of Agriculture

U.S. DOE = U.S. Department of Energy

(end of ATSDR excerpt)

## ***Detection of Ammonia Vapor in Air***

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There are several different methods in use for detecting and measuring ammonia concentrations in air. These methods range from simple stain-type detector tubes to ion chromatography. Measurement of ammonia concentration is important to several different groups of individuals. Atmospheric scientists are interested in the ammonia concentration in the atmosphere. They are normally measuring concentrations of 0.1 ppm or less. Industrial hygienists need to measure ammonia concentrations for Permissible Exposure Level (PEL) compliance verification. They are normally interested in concentrations in the 10–100 ppm range. Researchers testing the health effects of ammonia exposure with human or animal subjects typically are interested in measuring concentrations in the 25–2500 ppm range. Emergency response personnel are generally interested in measuring concentrations at high levels so that appropriate personal protective equipment is used and so that potentially flammable concentrations can be detected. They are normally interested in measuring concentrations in the 1–20 percent range (10,000–200,000 ppm). Detectors are also used to initiate alarms and start emergency ventilation equipment in the event of ammonia leaks. The different needs in terms of measurement speed, accuracy, and concentration range make various technologies more or less suitable for each application. The more widely used concentration measurement methods are:

- Capacitance
- Length-of-Stain Tubes
- Indophenol (Berthelot reaction)
- Ion chromatography
- Infrared spectrometry
- Gas-specific electrodes
- Electrochemical
- Semi conductor (solid state)
- Ultraviolet absorption

### ***Capacitance***

A polymer film functioning as a dielectric between two capacitor plates is the sensor. Alternate heating and cooling of the capacitor is accomplished by electrical heating which removes water molecules. Ammonia absorbed into the capacitor material changes the relative permittivity and thus the capacitance. As a result of the heating and cooling, the ammonia absorption causes a hysteresis affect that is proportional to the amount of ammonia present. This sensor has a reported measurement range of 0–1000 ppm (v/v) and requires periodic calibration.

### ***Length-of-Stain Tubes***

Probably the most frequently used concentration measurement method, stain tubes provide reasonably accurate indications of ammonia concentration. They are extremely simple to use and are quite inexpensive. There are two basic types of stain tubes in use. The first is a diffusion tube which relies totally upon diffusion of ammonia into the tube after one end of the tube is opened. A strip of impregnated paper in the tube changes color as the ammonia diffuses into the tube. The tube is calibrated so that the length of the stain can be determined after the sample time is completed. The stain length and the sampling time are used to determine the average concentration. These stain tubes require no pump and are best suited for measuring long-term average exposure such as would be used for an 8-hour time-weighted average exposure.

The second type of tube is one which is packed with impregnated beads which change from orange to blue as more ammonia enters the tube. A powered or manual pump is used to draw a known volume of air through the tube after both ends are opened. The tube is typically calibrated to read concentration directly provided that the nominal amount of air was drawn through the tube. The concentration can be adjusted accordingly if more

or less air was passed through the tube. These tubes are typically used for instantaneous concentration measurements since a reading can be obtained in about fifteen seconds. Tubes are available in several different ranges including the 0–10 percent range as well as the lower ppm ranges. Amines and other basic compounds can interfere with the measurement, appearing as increased concentration.

### ***Indophenol***

This method (also referred to as the Berthelot reaction) is the actual lab analysis method which is used after a sample has been collected in the field. There are several different sample collection methods in use. In the case of very low-level atmospheric concentration measurement, known volumes of air are drawn through a filter coated with oxalic acid which absorbs the ammonia. The resultant material is rinsed from the filter for analysis by the indophenol method.

In other cases the ammonia-containing air is bubbled through a dilute sulfuric acid solution in an impinger flask to prepare a sample for analysis. Another method uses low temperature condensation by drawing the sample through a dry ice/acetone bath which condenses the ammonia into liquid form. The condensation technique is reported to provide more accurate results than the acid absorption technique. Once the sample is prepared the indophenol analysis method can take place. This method is described in detail in *Patty's Industrial Hygiene and Toxicology* (1981).

### ***Ion Chromatography***

Ion chromatography requires the preparation of a field sample prepared by drawing the sample gas through a sampling tube containing carbon beads treated with sulfuric acid. A calibrated sampling pump is used. A normal sample time might be four hours with a total sample of 24 liters of air drawn through the tube. The tubes are then sealed and sent for lab analysis. In the lab the beads are desorbed with de-ionized water to get the correct total volume of solution. An ion chromatograph is used to develop chromatograms. These plots can then be used to determine the ammonia concentration.

### ***Infrared Spectrometry***

I.R. spectrometry is a good method for measuring instantaneous concentrations of ammonia and is particularly well suited to the higher concentration levels. These instruments are quite accurate and are not subject to interference or false readings from other gases. A sample is passed through a chamber and infrared light is passed through the chamber via narrow band pass filters which allow only a certain wavelength of light to pass. This is the exact wavelength which ammonia absorbs. The instrument measures how much of the light is absorbed by the gas sample and translates the absorption to concentration on a continuously updated basis. These devices are suitable for either fixed or portable use. They would make excellent combustible concentration alarm detectors for ammonia. They are able to measure concentrations very accurately at either high or low concentrations. They are relatively expensive instruments.

### ***Gas-Specific Electrodes***

The gas is drawn through a collection tube containing sulfuric acid-treated silica gel which captures the ammonia vapors. The ammonia is then desorbed with sulfuric acid. The resultant solution is then quantitated using a gas-specific electrode and a millivoltmeter. The electrode potential is indicative of the ammonia concentration.

### ***Electrochemical***

Electrochemical detectors use a liquid electrolyte enclosed in a housing with a permeable membrane that allows the ammonia vapor to come in contact with the electrolytic solution. Electrodes immersed in the electrolyte measure the change in potential which occurs when the ammonia permeates the membrane and dissolves in the solution. This type of detector is fairly selective to ammonia but is still sensitive to some other gases. It is very temperature sensitive. It is best suited to applications where the sample gas is drawn to the cell in a stabilized temperature environment. The cell must be zeroed and spanned with a reference gas. The life of the cell is quite short and cells are relatively expensive.

**Semiconductor (Solid State)** Solid-state detectors use a heated semiconductor which rapidly undergoes a change in its internal resistance when it comes in contact with ammonia vapor. These detectors are relatively inexpensive and rugged and the sensors have a relatively long life (1–5 years). The detectors have no moving parts and require no sampling method. The detector is simply mounted in the area in which the detection is to occur. These sensors are sensitive to other gases (CO, H<sub>2</sub>S, combustion gases, ethylene) and are sensitive to temperature changes. These sensors do not have the ability to reliably detect ammonia vapor at levels below 50 ppm.

**Ultraviolet Absorption** Ultraviolet absorption detectors operate on a principle similar to that used in the infrared spectrometry detectors. These detectors are quite accurate and are relatively insensitive to interference by other gases. A sample is drawn through a chamber where ultraviolet light is present. The detector measures how much of the ultraviolet beam is absorbed by the ammonia in the sample and converts that to concentration. These detectors are well suited for measuring concentrations in the 25–200 ppm range. They are relatively expensive but not as expensive as the infrared spectrometry detectors.

The sensor is rapidly heated and cooled during the measurement cycle, and ammonia is alternately absorbed and desorbed, causing hysteresis between the heating and cooling curves. Water molecules are also absorbed, but because sorption and desorption take place very rapidly measurements are unaffected by changes in humidity.

### ***Detection of Ammonia in Aqueous Solution***

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#### **Background**

One obvious method of detecting ammonia in a solution is by the presence of an ammonia odor. Even very weak solutions of ammonia will give off an easily detected odor when the solution is exposed to the air. The problem with this detection method is that the concentration of ammonia in the solution cannot be quantified. Because different people can have widely varying odor detection thresholds, presence of ammonia might not be detected if the odor-sensing is being performed by someone who has a relatively high odor threshold level for ammonia. This approach also is obviously not well suited to any automatic monitoring/alarm systems which require some form of digital or analog input.

Ammonia detection and measurement of concentration by objective, quantifiable means is facilitated by the fact that ammonia disassociates (or actually associates) quite completely when it is added to any aqueous (water-containing) solution. The ammonia molecules tie up hydrogen ions to form ammonium ions. This results in a decrease in hydrogen ion activity in the solution. Solutions with high levels of hydrogen ion activity are known as acids while solutions with low levels of hydrogen ion activity are known as bases or alkaline solutions. Lu and Fenton (2003) have reviewed and summarized detection methods for measuring ammonia concentration in aqueous solutions.

Fortunately, the acidity or alkalinity of a solution is quite easily measured and is expressed in terms of pH. As explained in the following paragraphs, pH is an excellent indicator of the presence of ammonia in a solution.



**Detecting Ammonia  
by Measuring pH**

The pH scale is a series of numbers (0–14) expressing the degree of acidity or alkalinity of a solution, as compared to some reference solution. The inventor of the term pH was named Sorensen and he defined it as:

$$\text{pH} = -\log [\text{H}^+] \quad (\text{negative log of hydrogen ion concentration})$$

A solution is neutral when all of the hydrogen ions are matched with hydroxide ions. At 25°C a neutral solution has a pH of 7.0. Aqueous ammonia solutions at the concentration levels of interest for typical situations will be in the pH range between 7 and 12. This part of the pH range is typically classified as weakly alkaline.

It is important to remember that pH is a logarithmic relationship to concentration if one assumes that the ammonia fully associates with hydrogen ions when it goes into solution. This means that the first amounts of ammonia going into solution will change the pH quite rapidly. As an example, if it takes one pound of ammonia to increase the pH of a solution from 7.0 to 8.0, then it will take ten pounds to go from 8.0 to 9.0, 100 pounds to go from 9.0 to 10.0, etc. The temperature of a solution does have some effect on pH but it is not a major factor unless the temperature swings are large.

Unlike the theoretical definition of pH, there is a more practical definition that is linked to the analytical method used to measure the pH of a solution. The basic principle of electrometric pH measurement is determination of the activity of the hydrogen ions by potentiometric (voltage) measurement using a standard hydrogen electrode and a reference electrode. However, because of difficulty in its use and the potential for poisoning the hydrogen electrode, the glass electrode is used for commercial pH monitors. The glass electrode, actually a membrane electrode, is comprised of a thin-walled bulb of special pH-responsive glass sealed to a stem of high resistance glass. The internal reference electrode is permanently immersed in a reference buffer solution of known pH. The voltage generated between the two electrodes is a direct indicator of the pH difference between the reference solution and the solution in which the glass electrode is immersed:

$$\text{pH} = \text{pH (ref)} + \text{voltage}/0.000198T \quad (T \text{ expressed in Kelvin})$$

At 25°C the theoretical pH values for aqueous ammonia solutions of varying concentration are as follows.

**TABLE 3-3**  
**Theoretical pH Values for Aqueous Ammonia Solutions**

Weight Percent	Normality	pH
17.000	10.000	12.1
1.700	1.000	11.6
0.170	0.100	11.1
0.017	0.010	10.6
0.0017 (17 ppm)	0.001	10.1

Note the very rapid jump in pH as a very small amount of ammonia is added to the water. This phenomenon makes it very easy to detect the presence of ammonia at very low concentrations by way of a pH measurement. Since most pH meters are accurate to the nearest 0.02 units, the resolution of the readings is quite good.

A pH monitor is comprised of the glass electrode sensor, the sensor leads, the electronic circuits to measure the voltage and convert to an analog indication, temperature compensation circuits (if needed), and any output circuitry for analog outputs or discrete alarm outputs.

Glass electrodes are quite durable and versatile. In normal use the electrode will perform for a year or more between replacements. It is not influenced by oxidizing or reducing agents nor is it affected by common electrode poisons. Electrodes are sometimes designed specifically for a range of temperatures. The normal pH range to be measured may also dictate the specific type of glass electrode that is best suited for an application. Most general purpose electrodes will be usable for the 7–12 pH range of interest for ammonia.

Since probes have a limited useful life they are typically configured so that they can be easily removed from the pipeline fitting/holder for replacement. Some of the lower cost electrodes are encased in a threaded plastic housing so that the housing, electrode, and cable are throw-away. Some electrodes incorporate battery powered pre-amplifiers that can transmit outputs up to 1000 feet to a recorder or multi-meter. Some glass electrodes incorporate automatic temperature compensation right in the electrode assembly. In other cases a separate RTD or thermistor sensor is used for temperature compensation. If a pre-amplifier is not used the pH transmitter must typically be located within 10 feet of the sensor. The transmitter normally incorporates the calibration adjustment and the temperature compensation capability. The transmitter output is normally a 4-20 mA signal which can be sent to a meter, recorder, data logger, or computer interface. The transmitter requires a 24 VDC power supply to function.

Typical general purpose glass electrodes with automatic temperature compensation are available from a number of suppliers. Pre-amplifiers increase the price. One limiting factor of the glass electrode pH monitoring approach is that the lowest available temperature range bottoms out at about 0°C. While this is not a problem for water-only applications, it precludes use on sub-freezing applications involving glycols or brines. In order to use the glass electrode pH meter on sub-freezing applications it is necessary to divert a small flow of the solution through an electric heating element to raise the temperature.

There are manual pH determination methods that can be performed which use colorimetry for detecting the presence of ammonia in aqueous solutions. Water testing kits are available which include specific test materials for ammonia detection in the ppm range. Salicylate is dissolved in a measured sample of solution and the degree of color change is compared to reference color shades for various ppm levels. Different kits are available for fresh water and salt water (brine) solutions. Since the commercially available ammonia test kits are designed to measure levels of 10 ppm or less, they will not be able to quantify how much higher the concentration might be. A narrow-range pH testing kit using alizarin yellow as the indicator allows pH measurements in the 9.7–11.6 range which would cover the higher concentration range.

## *Environmental Sampling*

Following is an excerpt from ATSDR Toxicological Profile for Ammonia (2004). Consult the *Toxicological Profile for Ammonia* for the references cited in that document as they are not repeated here.

Water and waste water samples can be analyzed for ammonia by EPA Test Methods 1689 (EPA 2001a), 1690 (EPA 2001b), and 349.0 (EPA 1997). Analogous procedures (i.e., Method APHA 4500) have been approved and published jointly by the American Public Health Association, American Water Works Association, and Water Pollution Control Association. These methods are suitable for drinking, surface, and saline waters, and domestic and industrial effluent, and can be applied to biosolids. These and other methods for determining ammonia in environmental samples are listed in Table 3-4. Ammonia is reported as ammonia nitrogen. Two methods that are suitable for water employ colorimetric techniques, Nesslerization, and phenate methods. Nessler's reagent, an alkaline mixture of mercuric and potassium iodide, produces a yellow to brown color with ammonia, whereas the phenate reagent, alkaline phenol, and hypochlorite produce a blue color (EPA 2001a, 2001b; Greenberg et al. 1985). In the titrimetric method, the distillate is titrated with standard sulfuric acid with an appropriate indicator. The ammonia electrode employs a hydrophobic gas-permeable membrane to separate the sample solution from an internal ammonium chloride solution: ammonia diffusing through the membrane changes the pH of the internal solution and is sensed by a pH electrode. For determining  $\text{NH}_3\text{-N}$  concentrations above 5 mg/L, the *titrimetric and ammonia-selective electrode* methods are preferred. In contrast, gas chromatography/mass spectrometry methods have been developed that permit  $\text{NH}_3$  detection at concentrations near 20  $\mu\text{g/L}$  for environmental waters (Mishra et al. 2001). Methods for determining ammonia in water and soil measure ammoniacal nitrogen, the sum of  $\text{NH}_3$  and  $\text{NH}_4^+$ . In the determination of ammoniacal nitrogen in soil, exchangeable ammonium should be distinguished from nonexchangeable ammonium. The former is usually defined as that which can be extracted with KCl (or  $\text{K}_2\text{SO}_4$ ) at room temperature (Bremner 1965). Nonexchangeable ammonium ion is defined as nitrogen held by clays and not displaced by 2M KCl (Bremner 1965). In the determination of nonexchangeable ammonium, organic forms of ammonia are first removed, the minerals containing the nonexchangeable ammonium are then decomposed with HF, and the ammonium ions released. In colorimetric procedures, turbidity and sample color may lead to interference. To eliminate interference, the pH of the sample may be raised and the ammonia distilled. Care should be taken to prevent losses in water samples due to volatilization and microbial transformation. To prevent such losses, samples should be acidified soon after collection and refrigerated. Care should also be taken during storage and treatment of soil samples to prevent ammonia loss or gain. It has been demonstrated that dry soil can rapidly adsorb trace amounts of ammonia from the atmosphere and that extensive amounts of ammonia can be lost during air drying (Bremner 1965). Additionally, in samples containing both ammonium and nitrite, losses during air drying may occur due to the reaction between these ions and the resulting formation and release of nitrogen gas (Bremner 1965).

**TABLE 3-4 Analytical Methods for Determining Ammonia in Environmental Samples**

Sample matrix	Preparation method	Analytical method	Sample detection limit	Percent recovery	Reference
Air	Passive collection using 0.01 N H <sub>2</sub> SO <sub>4</sub> in liquid sorbent badge	Method 6701, ion chromatography, conductivity detection	1 µg NH <sub>3</sub> /sample	No bias between 6.9 and 48 ppm; +19% at 148 ppm	NIOSH 1987
Air	Air samples from stack emissions collected through an in-stack filter to remove particulates and ammonium salts, and then bubbled through 0.1 N H <sub>2</sub> SO <sub>4</sub>	EPA Method 30; ion chromatography	1 µg NH <sub>3</sub> /sample	98.5±1.3%; Bias of 0.996 ppm for a spiked sample of 6.43 ppm. Correction factor of 0.87 needs to be applied	Eaton et al. 1996
Air	0.8 µm prefilter may be used; ammonia trapped on sulfuric acid silica gel	NIOSH method 6015, Colorimetric determination of indophenol by visible light spectrophotometry	0.5 µg NH <sub>3</sub> /sample	Not determined	NIOSH 1994
Air	0.8 µm prefilter may be used; ammonia trapped on sulfuric acid silica gel	NIOSH method 6016. Ion chromatography	2 µg NH <sub>3</sub> /sample	102±3.8%	NIOSH 1996
Air	Chromatomembrane cells preextract and preconcentrate sample	Ion chromatography with conductivity detection	6 µg NH <sub>3</sub> /sample	Not reported	Erxleben et al. 2000
Air	Collection in H <sub>2</sub> SO <sub>4</sub> coated activated carbon beads in sampling tube	Ion chromatography	2 µg NH <sub>3</sub> /sample	95–110% recovery	Bishop et al. 1986
Air	Known volume of air drawn through prefilter and H <sub>2</sub> SO <sub>4</sub> treated silica gel	NIOSH S347, ammonia-specific electrode	Not reported	97.6% mean recovery	SRI 1988
Water	Sample mixed with borate buffer	Method 1689, ion selective probe	0.1 mg/L	Not reported	EPA 2001a
Water	Sample collected, preserved with H <sub>2</sub> SO <sub>4</sub> , and chilled to 4°C. Samples should not be stored following reaction for >28 days	Method 1690, colorimetric determination of indophenol blue, of any ammonia with alkaline phenol and hypochlorite	0.2 mg/L	Not reported	EPA 2001b
Water	None	Method 350.1 colorimetric, automated phenate	0.1 mg/L	107 and 99% recoveries at 0.16 and 1.44 mg NH <sub>3</sub> -N/L, respectively	EPA 1983
Estuarine and coastal water	Samples filtered through 0.45 µm membrane filter, refrigerated and analyzed within 3 hours	Method 349.0, automated colorimetric determination by reactions that form indophenol blue	0.3 µg/L	92.2–109.1% recovery, n=14	EPA 1997a
Water	Removal of residual chlorine with sodium Nessler reagent, thiosulfate, distillation	Method 350.2 colorimetric, titrimetric ammonia specific electrode	0.05 mg N/L for colorimetric and potentiometric; 1.0 mg N/L for titrametric	28.12 to 0.46R bias between 0.21 and 1.92 mg N/L	EPA 1983
Water	None	Method 350.3 ion selective electrode	0.03 mg N/L	96 and 91% recoveries at 0.19 and 0.13 mg N/L, respectively	EPA 1983
Soil, exchangeable ammonium	Extract soil with 2N KCl	Method 84-3, steam distillation with MgO, titration	Not reported	Not reported	Bremner 1965
Soil, non-exchangeable (fixed) ammonium	Pretreat soil with KOBr-KOH, shake with 5 N HF-1N HCl for 24 hours	Method 84-7, steam distillation with KOH, titration	Not reported	Not reported	Bremner 1965

The detection limit of analytical methods for determining ammonia in air depends on the amount of air collected in a liquid or solid adsorbent. Sampling is performed with passive samplers or by drawing a volume of air through the adsorbent using a pump. Particulate contaminants such as ammonium salts may be removed by a prefilter. For determination of ammonia in the ambient atmosphere, larger volumes of air must be sampled than those appropriate for determinations of ammonia in occupational settings (e.g., industrial, agricultural) where ammonia levels are higher. Improvements in methodologies have led to development of techniques that permit continuous monitoring of atmospheric ammonia down to  $0.1 \mu\text{g}/\text{m}^3$  (Pranitis and Meyerhoff 1987). Several passive monitoring systems report detection limits of  $0.05$ – $1.0 \mu\text{g}/\text{m}^3$  and have collection rates ranging from  $2.7$  to  $2,000 \text{ mL}/\text{minute}$  (Kirchner et al. 1999). One method used for ambient atmospheric sampling employs a specially designed flow-through, ammonia-selective electrode with a sniffer tube, whereas the methods used for occupational settings often use passive collectors with media (usually acids impregnated onto filters) housed within protective cases. Ammonia concentrations on these passive collectors are then determined by a wide range of methods, including colorimetric assays (e.g., indophenol determination), the Berthelot reaction, or ion chromatography (Kirchner et al. 1999).

Ammonia may be present in air in both the vapor phase as ammonia gas and in the particulate phase as ammonium salts. While some analytical methods may distinguish between these phases, most standard methods do not. Methods have been developed that determine gaseous ammonia alone or gaseous and particulate forms of ammoniacal nitrogen separately. These methods use filter packs or sampling tubes coated with a selective adsorbent (denuder tube) to separate the phases (Dimmock and Marshall 1986; Knapp et al. 1986; Rapsomanikis et al. 1988). In these methods, gaseous ammonia is trapped by acids that act as adsorbents (e.g., citric acid, oxalic acid, phosphoric acid) on a coated filter or denuder tube (Kirchner et al. 1999). In filter methods, errors may arise due to ammonia interactions occurring on the filter and volatilization of retained ammonium salt (Dimmock and Marshall 1986; Rapsomanikis et al. 1988). There is evidence that ammonium nitrate in particulate matter is in equilibrium with ammonia. The presence of ammonium nitrate may lead to overestimation of the actual concentration of ammonia, but underestimation of the concentration of ammonium (Doyle et al. 1979). For additional review of the methodologies for determining ammonia in water and air, see MacCarthy et al. (1987) and Fox (1987), respectively.

(end of ATSDR excerpt)

### *Concentration in Vicinity of Vapor Release*

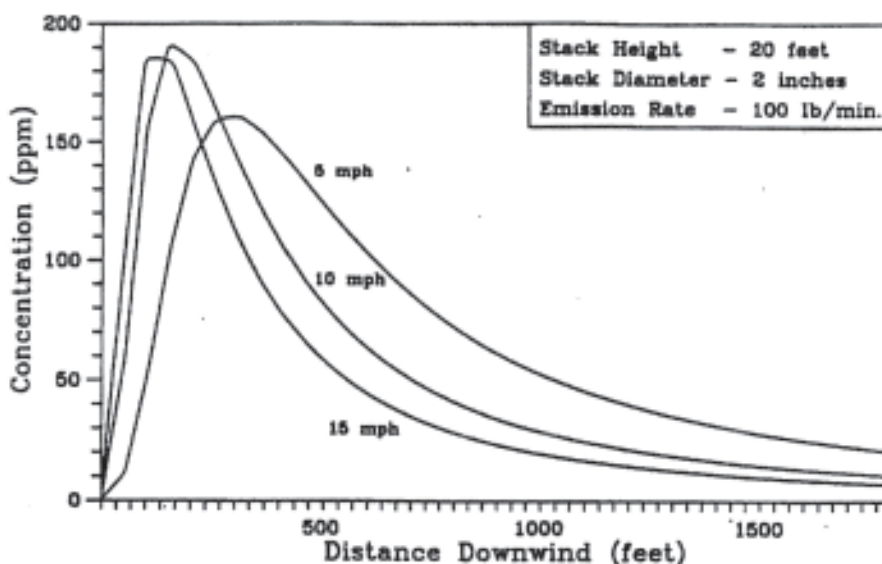
Ammonia is commonly stored in refrigerated atmospheric tanks or in non-refrigerated pressure vessels. In either case the tanks or pressure vessels must be equipped with safety pressure relief devices to prevent tank or vessel failures due to overpressure from abnormal situations. Such relief devices typically are designed to vent ammonia vapor from the tank or vessel at a rate sufficient to prevent excessive pressures in the containment vessel. Failure to provide such relief venting could result in catastrophic tank or vessel failure which could endanger the surrounding population. Controlled venting of ammonia vapor prevents such catastrophic releases of liquid and vapor. However, the venting of the vapor is still some cause of concern to those in the surrounding area.

IIAR has conducted research into the concentrations that could be expected when pressure relief valves of different sizes discharge ammonia vapor under a number of different conditions. A computer program was used to model a number of different atmospheric dispersion scenarios. The program incorporates the U.S. EPA's *Industrial Source Complex Short Term (ISCST) Model* (1987). Some generalized results of the modeling are summarized as follows for releases which are at least forty feet above ground level:

- Vapor release rates less than 75 pounds per minute will result in peak ground-level concentrations less than 100 ppm with the highest concentrations about 300 to 500 feet downwind of the release point. Concentration is roughly halved every additional 500 feet downwind.
- Vapor release rates greater than 75 pounds per minute will result in peak ground-level concentrations on the same order as the release rate (200 pound per minute release results in a peak concentration of about 200 ppm). The peak concentration occurs 400 to 600 feet downwind of the release point. Concentration is halved every additional 500 feet downwind.

Examples of the graphical presentation of concentration for two specific sets of conditions are shown in Figure 3-2.

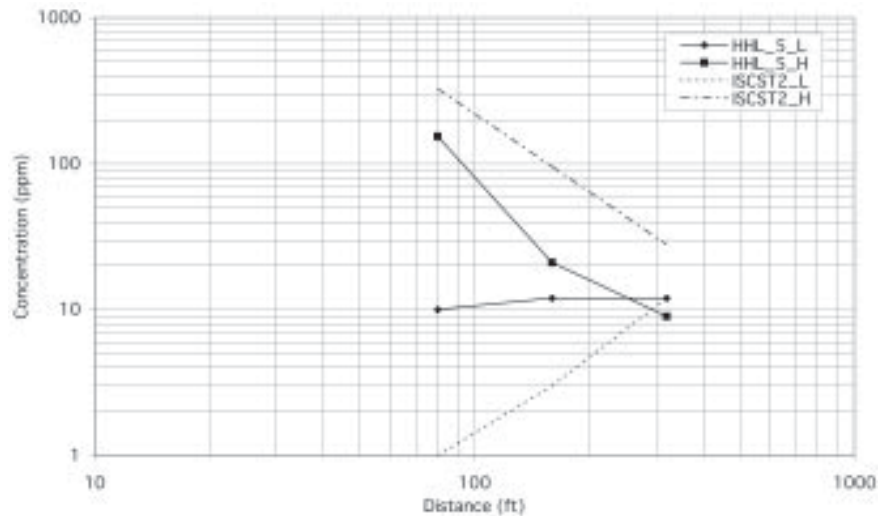
**FIGURE 3-2 Concentration vs. Distance Downwind of Stack**



Fenton (et al. 2001) conducted a series of experiments consisting of controlled ammonia vapor releases and the measurement of downwind ammonia concentrations. From these experiments, three vapor source characteristics were varied: elevation of release (6.5 ft and 26.5 ft), ammonia concentration in release stream (100% and 1% by volume), and upward velocity of the release flow (33 ft/s and 164 ft/s). Ammonia vapor detectors were placed at downwind distances of 80 ft, 160 ft, and 320 ft at elevations of 6.5 ft and 26.5 ft above the ground from the release point. During the conduction of these experiments, a database consisting of 81 releases was compiled.

A later version of the ISCST model, called ISCST2 Model (1992) was used by Fenton (et al. 2001) to predict ammonia vapor concentration in the plume using the experimental conditions as inputs. Over the 81 release data points, the ISCST2 predicts downwind concentration at ground level to within a factor of 2 or 3 for those conditions when the concentrations are greater than 10 ppm (v/v). For conditions within 5° of the ammonia plume centerline, ISCST2 tends to over-predict ammonia vapor concentrations. A typical result is shown in Figure 3-3 where the release conditions are: 100% ammonia vapor concentration, 26.5 ft elevation above ground, and 33 ft/s upward velocity. At a distance of 160 ft downwind from the release point, the predicted concentrations are about a factor of three below the measured values. At 320 ft downwind, the predicted and measured concentrations are within 30% of each other. For positions of 5° to 6° off the plume's centerline, ISCST2 closely predicts the measured concentrations.

**FIGURE 3-3. Comparison of predicted and measured downwind ammonia vapor concentration for release: 100% ammonia vapor concentration (H), 26.5 ft release elevation (H), and 32.8 ft/s upward velocity (L). [Last letter in chart label: L-ground level (6.5 ft), H-high level (26.5 ft)]**



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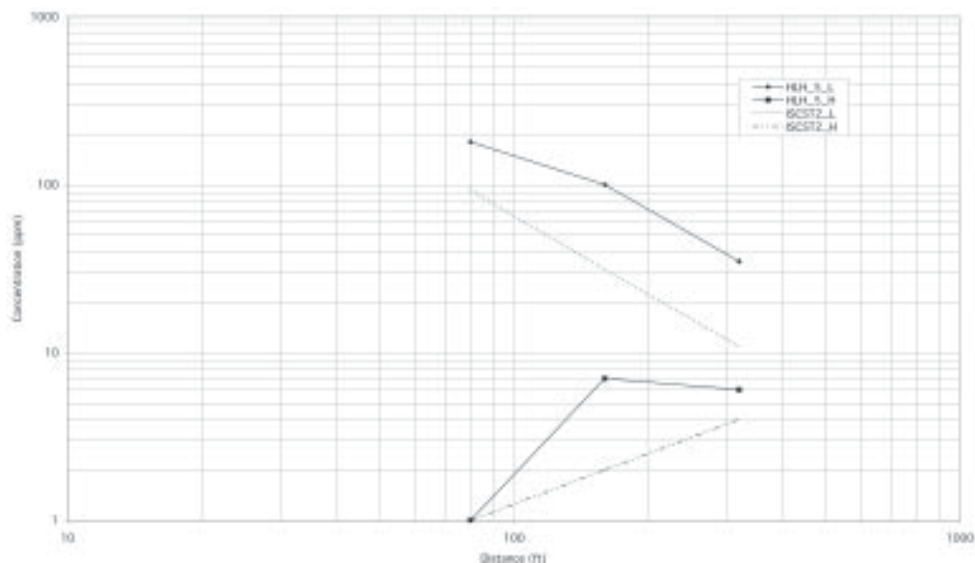
For positions greater than 10° off the plume's centerline, ISCST2 tends to under-predict downwind ammonia vapor concentrations. Figure 3-4 shows a typical under predicted result where the measurements were made at 7° off the plume's centerline. Overall, the database of the releases generalizes to the following three trends:

- Increasing the elevation of the release point by approximately a factor of 4 results in a reduction of the ground level ammonia vapor concentration by a factor of approximately 4.

- Diluting the ammonia vapor concentration by a factor of 100 (100% -to- 1%) results in the downwind ground level ammonia vapor concentration being reduced by a factor of approximately 2.
- Increasing the upward velocity of ammonia flow by a factor of 5 reduces the downwind ground level ammonia vapor concentration by about 1.3.

Over the range of experimental conditions tested by Fenton (et al. 2001), the elevation of the release point was the most significant variable tested influencing the downwind ground level ammonia vapor concentration.

**FIGURE 3-4. Comparison of predicted and measured downwind ammonia vapor concentration for release: 100% ammonia vapor concentration (H), 6.5 ft release elevation (L), and 164 ft/s upward velocity (H). [Last letter in chart label: L-ground level (6.5 ft), H-high level (26.5 ft)]**



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A release of pressurized liquid ammonia to the atmosphere results in the generation of vapor cloud also. Prediction of downwind ammonia concentration in such release scenarios has been addressed in the *Guidelines for Evaluating the Characteristics of Vapor Cloud Explosions, Flash Fires and BLEVEs* (AIChE 1994). Mention is also made (Fleischer 1980) of the situation where a pool of boiling liquid is generating a vapor cloud. The 1985 desert test release of ammonia (Goldwire et al. 1985) may also be of interest to the reader.



## ***U.S. EPA 2005 Toxics Release Inventory Data***

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As described in *Chapter 5 — U.S. Regulatory Requirements* of this Data Book, SARA Title III regulations require facility owners to file an annual report (Form R) with U.S. EPA which discloses the annual release of ammonia to the environment (SARA 1986). All of the Form R data submitted is then accumulated and summarized in an annual government report (EPA 2005). Some of the highlights of the 2005 report are presented:

- All American industry categories reported total fugitive and stack ammonia releases to the atmosphere of 119,000,000 pounds in 2005. That same year, a total 159,000,000 pounds of ammonia was released to the environment (air, water, and land). Interestingly, the entire quantity of ammonia released to the environment equates to less than 0.5% of that year's total reported U.S. consumption of ammonia. The 2005 0.5% level of ammonia releases is significantly reduced from the 2% level in 1990. (It should be noted that agricultural application of ammonia is not included in these release figures.)
- The most-released chemical in 2005 was hydrochloric acid at 565,000,000 pounds.
- The grand total of all toxic chemicals released to the environment was 4,339,000,000 pounds in 2005. Ammonia represented about 4% of the total.
- Over the period from 1988 to 2005, food facilities (industry category SIC 20) emitted ammonia to the atmosphere ranging from a low in 2004 of 11,970,000 pounds to a high of 24,020,000 pounds in 1997. For 2005, the total annual emission of ammonia by food facilities to the atmosphere in the United States was 12,000,000 pounds.
- In 2005, total fugitive emissions of ammonia was 24,876,000 pounds, or 21% of the total emitted to the atmosphere. During the same year, total stack emissions of ammonia to the atmosphere was 94,000,000 pounds, or 79% of the total ammonia emitted to the atmosphere.
- Discharge of ammonia to surface water (streams, rivers, lakes, oceans, and other bodies of water) was 5,413,000 pounds in 2005. In 1998, the discharge of ammonia to surface water was significantly higher at 7,792,000 pounds.

## ***Effects of Ammonia on Food Products and Seeds***

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This section is taken from TRRF Research Summary #87-3, August, 1987, *Ammonia Spills and the Effect of Ammonia on Products Stored in Refrigerated Warehouses* by Michelle Smith, University of Maryland, prepared for The Refrigeration Research Foundation (TRRF). Reprinted with permission from the World Food Logistics Organization.

Much has been learned about the safety and handling of ammonia through its long history of use as a refrigerant. However, accidents still happen. If an ammonium leak or spill occurs in an area where product is being held, that product may be injured. This degree of damage resulting from exposure to ammonia is determined by many factors. The concentration of ammonia, length of exposure, temperature, type of product and manner in which the product is packaged all influence the extent of ammonia injury (Brennan et al., 1962; Rose, 1939; Woodstock and Tsao, 1986). Long term exposure to ammonia at low concentrations may be as damaging as short term exposure to higher concentrations (Blanpied and Smock, 1982). In the case of horticultural products — variety, quality, moisture content and even where a product was grown may influence susceptibility (Dewey, 1952; Woodroof, 1979; Woodstock and Tsao, 1986).

### **Mechanisms of Ammonia Injury**

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The mechanisms involved in ammonia injury have not been fully elucidated. Ammonia enters fruit through the lenticels, stem, breaks in the skin or directly through the skin. It combines with water in the product to form ammonium hydroxide. As cell sap pH becomes more alkaline, anthocyanins in fruit such as apple change from red to blue (Brennen et al., 1962) and anthoxanthins in yellow onions become brown (Ramsey and Butler, 1928). Tannins in nut shells or seed coats become dark brown or black (Dewey, 1952; Kays, 1982; Woodroof, 1979). Depending on the type of product and the level of exposure, discoloration may disappear upon aeration as cell sap pH returns to normal (Dewey, 1952). Changes in pH may also increase membrane permeability (Woodstock and Tsao, 1986). Severe ammonia injury is evidenced by browning due to oxidation reactions within damaged cells. Such injury may not become apparent until several days after exposure to ammonia, occasionally being masked by discoloration or because this type of injury develops more slowly (Harvey et al., 1972).

There is evidence that, in addition to its effect on cell sap pH, ammonia may be involved in metabolic reactions. Ammonia injury tends to increase with increasing temperatures and moisture contents (Kays, 1982; Woodroof, 1979; Woodstock and Tsao, 1986). There is also evidence that susceptibility may be greater in products with higher respiration rates. If ammonia injury or uptake are related to metabolism, then colder temperatures and lower moisture contents could be expected to reduce the amount of ammonia absorbed or metabolized, thereby, reducing injury (Woodstock and Tsao, 1986).

## Food Product Injury

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Slight injury may be indicated by a brown to greenish-black discoloration of the outer tissues of fruits and vegetables. Severe injury may be marked by discoloration and softening of the deeper tissues (Hardenburg et al., 1986). Acid products such as onions and products high in fat such as nuts are especially susceptible to ammonia injury (IARW, 1981; Ramsey and Butler, 1928).

Susceptibility to ammonia injury varies widely among plants and plant parts. Barton (1940) investigated the tolerance of living plants and seed to ammonia. He exposed tomato, buckwheat and tobacco plants to 0.1 percent (1,000 ppm) ammonia vapor. The leaves of these plants showed signs of serious injury within 3 to 8 minutes of exposure to ammonia. Stems were more resistant, requiring up to 8 hours of exposure to 0.1 percent ammonia to exhibit injury symptoms.

Ammonia injury in apples begins at the lenticels where gas enters the fruit and radiates outward. The anthocyanins of the skin serve as an indicator of the alkaline reaction. This reaction in red apples may be particularly striking as the fruit turns dark blue, purple or black. Yellow or green apples may become light brown when exposed to ammonia. Lenticels may become more prominent, assuming a “corkey” appearance (Blanpied and Smock, 1982; Brennan et al., 1962). Apples may recover with only minimal damage at the lenticels if aeration is quick and complete, providing ammonia dosage is low. However, apples which have been exposed to ammonia vapors will ripen more rapidly than normal and be more susceptible to fungal attack. Such apples should be moved into marketing channels as quickly as possible (Blanpied and Smock, 1982).

Brennan et al. (1962) investigated the effects of ammonia concentration and length of exposure on several apple and peach varieties. Fruits were compared as to extent of injury and concentration of ammonia absorbed. They found Red Rome and Red Delicious apples were particularly susceptible to ammonia injury followed by Stayman and Regular Rome; Paragon and Golden Delicious appeared to be the least sensitive. Golden Delicious presented an interesting problem in assessing ammonia damage. As they are grown in New Jersey, Golden Delicious apples characteristically have enlarged “corkey” lenticels. There was no change in appearance of these apples following exposure to ammonia. Therefore, this variety was assumed to be tolerant. By comparison, Golden Delicious apples grown in Washington State have a smooth, unbroken skin with lenticels that are barely visible. When exposed to ammonia, these apples showed blackening around the lenticels which progressed to the development of prominent “corkey” lenticels; indicating sensitivity to ammonia.

In peach, ammonia injury was seen as an over-all blackening which faded at the lower ammonia concentrations and progressed to a brownish, bruised appearance at higher rates of exposure. Blake and Red Crest varieties showed discrete spots as well as the larger bruised patches. Brennan et al. (1962) found no significant differences in susceptibility among the peach varieties they tested. As a group, peaches were more susceptible to ammonia injury than apples.

Dewey (1952) exposed various stone fruits to 1,000, 3,000 and 10,000 ppm ammonia for 1/2 hour at 35°F (1.7°C). Type of product had a significant impact on the degree of injury observed. Sweet cherries became dark blue at the lenticels when exposed to 1,000 ppm NH<sub>3</sub>. There was a gradual disappearance of discoloration upon aeration. Nectarines were also injured by the minimum NH<sub>3</sub> exposure (1,000 ppm). Injury symptoms included a discoloration of blush from red to blue or black and occasional

discoloration of non-blushed areas. Discoloration decreased upon aeration. Nectarines became brown and russeted when exposed to 3,000 ppm or higher concentrations. Peaches required a minimum exposure of 3,000 ppm  $\text{NH}_3$  to cause injury. Injury symptoms in peaches were similar to those in nectarine. However, permanent damage as browning became evident several days after peaches had been exposed to ammonia. Pears were the most resistant. Pears showed no immediate signs of injury when exposed to concentrations of up to 10,000 ppm  $\text{NH}_3$ . However, pear lenticels became dark blue subsequent to exposure and became brown after several days of storage at 70°F (21.1°C).

Dewey (1952) found varieties as well as commodities differed greatly in their response to ammonia exposure. Lenticels of Santa Rosa plums exposed to 1,000 ppm  $\text{NH}_3$  became swollen and discolored. Upon aeration, lenticels became sunken and dark brown. However, Wickson plums showed no signs of injury at the maximum ammonia exposure (10,000 ppm) used in this study. Cardinal grapes exposed to 5,000 ppm  $\text{NH}_3$  immediately showed signs of fruit and stem injury. Thompson Seedless, Black Monukka and Flame Tokay varieties were somewhat less susceptible, requiring 1,000 ppm  $\text{NH}_3$  exposure for 1 hour to cause fruit and/or stem injury. Emperor grapes showed no signs of fruit injury after 1.2 hour exposure to 20,000 ppm  $\text{NH}_3$  but stem injury was immediate.

In grapes, fruit became discolored primarily around the capstem attachment and at punctures or breaks in the epidermis. Stems became blue at scattered areas, especially at breaks and wounds. Aeration resulted in some dissipation of discoloration, but, permanent damage as evidenced by browning and pitting of fruit and stem tissues became apparent. The symptoms of ammonia injury on cherries, Santa Rosa plums and pears occurred at the lenticels. Injury on peaches and nectarines was not confined to any particular area of the fruit surface.

Color, size and flavor are important quality attributes in the grading of nuts. Nuts are prone to absorbing foreign odors present in their storage environment and nut quality will be reduced accordingly (Briston, 1945; Woodroof, 1979). However, the greatest concern appears to be the effect of ammonia on nut color. Exposure to ammonia gas may have little effect on the flavor, texture or nutritive value of nuts but, if discoloration is severe, nuts will be unmarketable from an aesthetic standpoint (Briston, 1945; Dewey, 1952; Kays, 1982; Medlock, 1931; Woodroof, 1979).

Woodroof and Heaton (1966) exposed several types of nuts to low but detectable levels of ammonia gas for 48 hours. Ammonia injury was seen as darkening or blackening of the testa. Susceptibility varied with the type of nut. Chestnuts showed the greatest degree of injury followed by pecans, filberts and Brazil nuts. Almonds, black walnuts and apricot nuts were also discolored but to a lesser degree. Peanuts were least susceptible to ammonia injury.

Rose (1979) examined the effects of concentration of ammonia gas and length of exposure at 32°F (0°C) on pecan, English walnuts and almond kernels. Pecans and almonds showed signs of injury within 15 minutes when exposed to 0.25 percent  $\text{NH}_3$ . At 0.10 percent  $\text{NH}_3$ , injury was not seen until after nuts had been exposed for 3 hours. English walnuts were less sensitive, requiring approximately 3 hours exposure at 0.50 percent  $\text{NH}_3$  and much longer concentrations to exhibit injury symptoms. Peanuts appeared to be unaffected by any of the concentrations (0.01 or 5.0 percent  $\text{NH}_3$ ) used in this study.

The persistence of discoloration in nuts is well documented (Dewey, 1952; Richardson and Meheriuk, 1982; Woodroof, 1979). Rose (1939) took nuts which had been exposed to from 0.01 to 0.06 percent ammonia gas and allowed them to aerate at 70°F (21.1°C) for 3 to 7 months. After 3 months, discoloration faded from almond shells and from walnut and almond kernels exposed to 0.02 percent NH<sub>3</sub>. Walnut kernels exposed to 0.04 percent NH<sub>3</sub> or higher concentrations recovered by 7 months. Almond kernels exposed to higher concentrations did not recover. Pecan kernels remained discolored after 7 months aeration regardless of the NH<sub>3</sub> concentration to which they had been exposed. Darkening was most severe in pecans which had been exposed to higher concentrations of ammonia.

Dewey (1952) exposed in-shell almonds, filberts, Persian walnuts, pecans and peanuts to concentrations of ammonia gas (10,000 to 100,000 ppm) sufficient to cause injury. In most cases, shell injury was apparent within the first 1/2 hour of exposure to relatively low concentrations (10,000 to 20,000 ppm) of ammonia gas at 35°F (1.7°C). Compared to the shells, nutmeat injury in in-shell nuts became apparent only after longer exposure and/or exposure to higher concentration of NH<sub>3</sub> at higher temperatures. This may have been due, in part, to the protective function of the shell. Woodroof (1979) reported that shelled pecans were approximately four times as sensitive to ammonia injury compared to in-shell nutmeats.

### **Factors Affecting Degree of Injury**

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Product Quality plays a significant role in susceptibility to ammonia injury. Brennan et al. (1962) found that newly harvested apples were more resistant to ammonia injury than apples which had been stored for many months. The reason for increased susceptibility following storage is uncertain. Many progressive changes have been associated with storage. These include decreased acidity and changes in the pectin fractions which cause softening. Woodroof (1979) also reported an increased sensitivity to ammonia in stored nuts. As the testa or kernel covering began to age, nuts became more susceptible to darkening by ammonia. In addition, poorly filled, damaged or shriveled nuts were more prone to darkening by ammonia compared to well filled, plump, fresh nuts.

Packaging has a dramatic effect on the degree of product injury caused by exposure to ammonia. In-shell pecans in bulk package burlap bags and tote boxes were severely damaged when exposed to ammonia gas in a commercial refrigerated warehouse. Injury was most severe in pecans closest to the surface. Shelled pecans in plain corrugated boxes were also subject to ammonia injury. Degree of darkening was slightly less when heavier weight cardboard was used. Waxed corrugated boxes offered more protection than plain corrugated boxes. Polyethy, cellophane, saran, laminated aluminum foil and nylon film were effective barriers against ammonia gas, provided the packages were well sealed (Woodroof, 1979). These results were in good agreement with earlier studies by Briston (1945). Briston concluded that any material capable of protecting against changes in moisture content due to fluctuating humidity would also tend to protect against ammonia fumes.

Hruby et al. (1983) studied the protective effect of packaging with respect to quality changes in a variety of frozen foods. The foods and packaging materials were as follows: 1. Apple puree in an unsoftened, polymerized vinylchloride (PVC) dish with a heat-sealed aluminum foil lid, 2. Strawberry and apple pulp in a PVC dish with a heat-sealed aluminum foil lid, 3. Fruit pulp in a PVC cup with a press-in PVC lid, 4. Spinach puree in a heat-sealed polyethylene bag, 5. Mixed vegetables in a polyethylene bag which was imperfectly sealed at the corners and 6. Ice cream

in a paraffin coated cardboard box. Each product, with and without packaging, was exposed to ammonia fumes for up to 24 hours in a desiccator held at 0°F (-18°C). Samples were periodically withdrawn to determine the concentration of ammonia absorbed. Sensory evaluations were performed to determine the concentration of ammonia absorbed which rendered a product unacceptable in terms of flavor, odor and color.

All unpacked frozen foods were significantly affected by exposure to ammonia. Thawing was observed as a result of lowered melting points. After 6 hours of exposure, a gelatinous layer began to form on the surface of the apple puree, possibly due to deesterification of pectins. This gelatinous layer was 5 to 7 mm thick after 24 hours of exposure to ammonia fumes. Unpackaged foods rapidly became unacceptable in terms of flavor, usually within 15 minutes to 1 hour of exposure to NH<sub>3</sub>. Color and/or odor changes were not detected until products had absorbed higher concentrations, normally within the first 1 to 3 hours of exposure. The fruit pulp and purees became red-brown. Spinach puree became dark green to brown. Except for the cauliflower florets, which turned brown, mixed vegetables did not exhibit any significant color changes. This in spite of the fact that mixed vegetables, with a relatively high surface area, absorbed the highest concentration of ammonia compared to other products. No color changes were seen in the ice cream used in this study. Ammonia will discolor some flavored ice cream such as black raspberry which turns blue (Kosikowski, 1986).

Hruby et al. (1983) found that well-sealed polyethylene and PVC packaging offered good protection against ammonia fumes when frozen foods were exposed for up to 24 hours. Mixed vegetables in an imperfectly sealed polyethylene bag were found to be unacceptable by virtue of an ammonia flavor within approximately 6 hours of exposure to ammonia. Paraffin coated cardboard offered very little protection against ammonia fumes.

Kassem and Johnston (1965) reported that frozen ground beef, strawberries and green beans were downgraded by a sensory panel following exposure to ammonia fumes. Ammonia adversely affected the color, flavor and texture of all products, with one exception. The color of green beans exposed to ammonia was rated superior to untreated green beans. Of the packaging materials tested, waxed paper offered the least protection against ammonia. Cryovac packaging was the best.

In another study, Herrmann and Johnston (1966) investigated the effects of ammonia on frozen beef and pork musculature. They found that ammonia was absorbed throughout the samples, although the highest concentration was found in the outer 1/4 inch layer. Ammonia odor and flavor were limited to the outer 1/4 inch of beef and pork samples. However, panelists noted an atypical flavor which was detectable throughout the beef samples. Ammonia had a slight tenderizing effect on beef. Color of beef and pork did not appear to be affected by exposure to ammonia. In the earlier study, Kassem and Johnston (1965) had found ammonia caused graying in ground beef. They suggested that the greater surface area of ground beef contributed to color changes in the meat.

Ting and Henrickson (1986) exposed frozen ground beef to liquid ammonia for 72 hours. Ammonia exposure resulted in an increased water holding capacity of the meat in both raw and cooked samples. A greater water holding capacity at more alkaline pH could explain the increased tenderness in beef following exposure to NH<sub>3</sub> reported by Kassem and Johnston (1965). Ting and Henrickson (1986) also exposed frozen ground beef packaged in polyethylene, cryovac and waxed paper

to liquid ammonia for 60 hours at 10°F (−12.2°C). All packages were heat-sealed. Sensory evaluation found the odor of all meat exposed to ammonia was inferior to that of the control. Odor was most objectionable when polyethylene had been used. Samples packaged in waxed paper were least acceptable in terms of flavor followed by polyethylene and then cryovac, although, none were significantly different from the control. Hunter L, a and b determinations and sensory evaluation showed no significant differences in the color of meat exposed to ammonia compared to untreated meat.

Lindborg (1980) reports that it is normally not possible for a sensory panel to detect residual ammonia in meat samples after thawing and cooking. Products with a heavy water glaze (e.g., glazed flounder, scampi and squid) will absorb ammonia but can be made edible by thawing, washing and cooking (Goodfellow et al., 1978).

### Seeds and Seedlings

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The use of cold storage is not limited to food items. Other commodities such as seed and nursery stock may be stored in warehouses which utilize ammonia as a refrigerant. These items may also be susceptible to ammonia injury. The toxic effect of ammonia on seedlings has been well documented (Allred and Ohlrogge, 1964; Grosse and Schmidt, 1980; Pal and Ojha, 1966; Tyagi, 1983; Woodstock and Tsao, 1985). Much of this work was based on fertilizers and animal waste as the source of ammonia but could conceivably be applied to cold storage situations.

Woodstock and Tsao (1986) investigated the effects of ammonia vapor on corn, soybean and peanut seed stored at 41°F (5°C) and 77°F (25°C). High concentrations of ammonia (2,000 to 20,000 ppm) reduced germination and seedling growth. Damage was greater at 77°F than at 41°F. Corn seed was the most sensitive to ammonia injury. They observed that corn readily absorbed ammonia and that corn release ammonia more slowly during aeration compared to soybean and peanut seeds. Soybean seed was the least sensitive. The quality of dry seed was not affected by exposure to 20 to 200 ppm NH<sub>3</sub> for 24 hours. Woodstock and Tsao concluded that the levels of ammonia most likely to be found following a leak (20 to 200 ppm) would probably not affect the growth or germination of soybean, corn or peanut seed but pointed out that it is possible that long term, low level exposure could be toxic. Seeds with higher moisture contents could also be more susceptible. Woodstock and Tsao reported that electrolyte release (as monitored by the ASAC-1000) was highly correlated with seedling growth and could therefore be used to detect ammonia injury in dry seed. Tyagi et al. (1983) investigated the effects of ammonia fumes (5, 10, 15, 20, and 50 ppm) on the germination and growth of cucumber seeds. Ammonia injury was characterized by a lower percent germination and a reduced speed of germination. However, seed exposed to less than 20 ppm NH<sub>3</sub> which did germinate showed an increased root and shoot length compared to untreated seed. At 50 ppm, ammonia was toxic to seed. The growth of five day old seedlings was inhibited by ammonia concentrations as low as 5 ppm. The effects of ammonia on cucumber seedlings became more severe with increasing concentrations, becoming lethal at 20 ppm.

### Assessing Ammonia Damage

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If a product is directly contaminated by liquid ammonia, that product is normally considered a total loss (Lindborg, 1980). It may be more difficult to determine whether products further from the source of an ammonia leak are contaminated. The technical literature offers little guidance concerning the evaluation of product quality following exposure to ammonia (Goodfellow et al., 1978).

The U.S. Food and Drug Administration (FDA), Bureau of Foods, Plant and Protein Technology Branch recommends several tests for assessing ammonia damage in exposed products. These methods include:

- Ammoniacal Nitrogen determination — Association of Official Analytical Chemists (AOAC) method 2.057. The maximum acceptable level of ammoniacal nitrogen does not normally exceed 0.15 percent.
- Sensory evaluation — A panel score of 5.0 or higher on a 9 point hedonic scale may be considered acceptable.
- pH measurement of contaminated food — Based on sensory evaluations, a product is generally considered acceptable if its pH does not exceed that of the normal product by more than 1.0 pH unit.
- Visual evaluation of the product — Ammonia may render a product unmarketable from an aesthetic stand point.

Reaction with Nessler's Reagent (Phillips, 1985) and ninhydrin (Porrit and Lidster, 1979), absorbance (Cralley et al., 1975), total kjeldahl nitrogen (Brennan et al., 1962), ammonia-selective electrodes (Hruby et al., 1983; Parris and Foglia, 1983) and enzymatic assays (Parris and Foglia, 1983) have also been used to detect ammonia residue in foods.

The FDA suggests that decisions regarding the acceptability of foods which may have been exposed to ammonia be based on at least three different test methods and that data be compared to control product data. Disposition decisions based on any single test parameter could be in error. The visual symptoms of ammonia injury on stone fruit, especially several days after exposure, may be similar to those of exposure to other materials (e.g., fumigants and detergents) commonly used in the postharvest environment (Phillips, 1985). Increases in pH may not be proportional to the concentration of ammonia absorbed due to the natural buffering capacity of foods (Kassem and Johnston, 1965; Ting and Henrickson, 1986). Brennan et al. (1962) found elevated nitrogen levels in apple and peach skins immediately after fruit were exposed to ammonia fumes. However, these elevated levels did not persist for more than a few days. They suggest that the value of chemical nitrogen analysis as a diagnostic tool is limited unless used soon after product has been exposed to ammonia. In addition, elevated ammonia levels in some foods (e.g. meats and seafood) may be the result of aging or microbial spoilage rather than exposure to ammonia fumes (Brooks and Ammerman, 1978; Parris and Foglia, 1983).



A simple qualitative method for detecting ammonia residue in stone fruit was described by Phillips (1985). According to this method, 5 gram samples of outer tissue (3 mm deep) are placed in a test tube containing 10 ml 8M NaOH. The mixture is heated to evolve ammonia but not boiled. Filter paper moistened with Nessler's Reagent and pH paper moistened with distilled water are exposed to gases in the test tube for 60 seconds. A basic pH (9-10) or a browning of the Nessler's Reagent is considered a positive indication of the presence of ammonia. This test was applied to control fruit purchased through normal retail channels and to fruit which had been exposed to 6 percent ammonia gas for 2 hours. It successfully identified contaminated fruit when performed 1, 7 and 14 days after treatment.

Goodfellow et al. (1978) used a combination of pH, ammoniacal nitrogen and sensory evaluation to assess the quality of frozen foods which had been exposed to ammonia in commercial storage. With few exceptions, a product was accepted only if its pH did not exceed normal product pH by more than 1.0 pH unit, its ammoniacal nitrogen content did not exceed 0.10 percent and its panel score was 5.0 or higher on a 9 point hedonic scale. Acceptance criteria for product pH and ammonia content were based on the results of sensory evaluation. They found microbiological testing was of little value unless there was evidence of thawing in a product. It has been reported that exposure to ammonia may actually reduce the number of viable microorganisms in a product (Goodfellow et al., 1978).

The only test performed by regulatory agencies on food which may have been contaminated during an ammonia leak is a sensory evaluation. If an ammonia odor or flavor is present the food is considered adulterated and therefore, unfit for human consumption. It has been observed that shrimp and other seafood are especially prone to absorbing ammonia. If aeration and/or repackaging is successful (i.e., ammonia odor is no longer detectable) the product may be salvaged (Anon, 1987).

(end of TRRF excerpt)

## *Effects of Ammonia on Aquatic Life*

The EPA's *Summary Review of Health Effects Associated with Ammonia; Health Issue Assessment* (1989) and its updates in 1998 and 1991 address the subject of aquatic toxicity. Following is a brief summary of the information presented in those documents.

Ammonia is recognized as being toxic to various kinds of aquatic organisms. In fact, the EPA established the reporting quantity for ammonia (100 pounds) because of aquatic toxicity. The EPA has established a maximum level of unionized ammonia in U.S. waters at 0.02 mg/L which is analogous to 0.02 ppm. When reference is made to ammonia concentration in water it is important that the form of the ammonia be identified. In aqueous solution ammonia is present in both unionized ( $\text{NH}_3$ ) and ionized ( $\text{NH}_4^+$ ) forms. The percentage of total ammonia present in the unionized form and its toxicity to aquatic organisms is highly dependent upon the pH and temperature of the water. As pH and temperature increases, the ammonia equilibrium is shifted toward the unionized  $\text{NH}_3$  chemical specie, thus increasing toxicity in most situations.

The acute toxicity of ammonia to fish has been widely studied (Thurston et al., 1984; Ruffier et al., 1981; European Inland Fisheries Advisory Commission, 1973). Acute median lethal concentration  $\text{LC}_{50}$  (mg/L) values for saltwater and freshwater fish tend to fall in the 0.3 to 3.0 range. Most of the tests were in flow-through conditions for 24 or 96 hours. It should be noted that these concentrations are unionized ammonia. Total ammonia concentration would be much higher.

There is much less data available on the effects of subacute and chronic exposure. Table 3-5 represents the estimated 32 day no-observed-effect-concentration for growth effects in smallmouth bass.

**TABLE 3-5**  
**Growth Effects in Smallmouth Bass**

pH	Total $\text{NH}_3$	Unionized $\text{NH}_3$
6.6	17.4 mg/L	0.0437 mg/L
7.3	14.4	0.148
7.4	14.6	0.599
8.7	2.4	0.612

Aquatic invertebrates are generally less sensitive than fish to ammonia exposure. Acute median lethal concentrations for a number of different invertebrates (such as snails, clams, crayfish, etc.) range between 1.1 and 10.1 mg/L expressed as unionized ammonia. The EPA 1998 Ammonia Update concerns the chronic criterion which was shifted from primarily dependent on pH to a combination of pH and the presence of early life stages of fish. The 1999 EPA Ammonia Update integrates comments received from the 1998 Ammonia Update where the "new criteria reflect research and data since 1984, and are a revision of several elements in the 1984 Criteria, including the pH and temperature relationship of the acute and chronic criteria and the averaging period of the chronic criterion. As a result of these revisions, the acute criterion for ammonia is now dependent on pH and fish species, and the chronic criterion is dependent on pH and temperature. At lower temperatures, the dependency of chronic criterion is also dependent on the presence or absence of early life stages of fish."