

6. POTENTIAL FOR HUMAN EXPOSURE

6.1 OVERVIEW

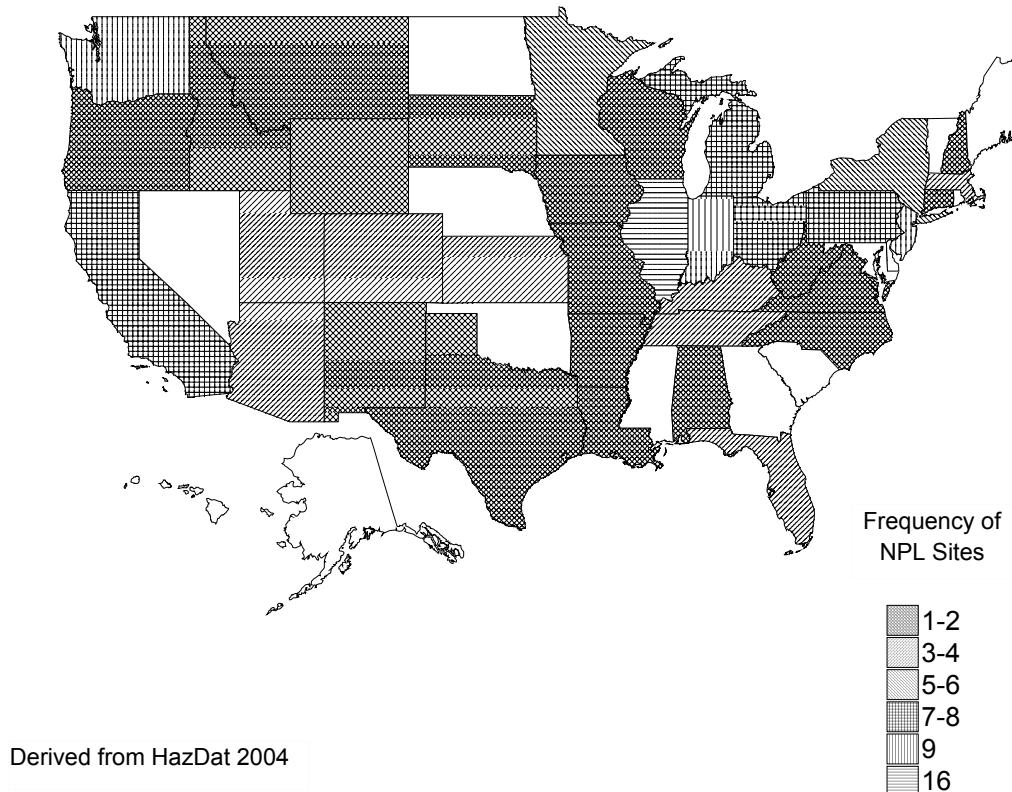
Ammonia has been identified in at least 137 of the 1,647 hazardous waste sites that have been proposed for inclusion on the EPA National Priorities List (NPL) (HazDat 2004). However, the number of sites evaluated for ammonia is not known. The frequency of these sites can be seen in Figure 6-1. Of these sites, 135 are located within the United States and 2 are located in the Commonwealth of Puerto Rico (not shown).

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 N₂ to other forms by different processes. Nitrogen fixation (the process of converting atmospheric N₂ to NH₃) 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 NH₃ 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.

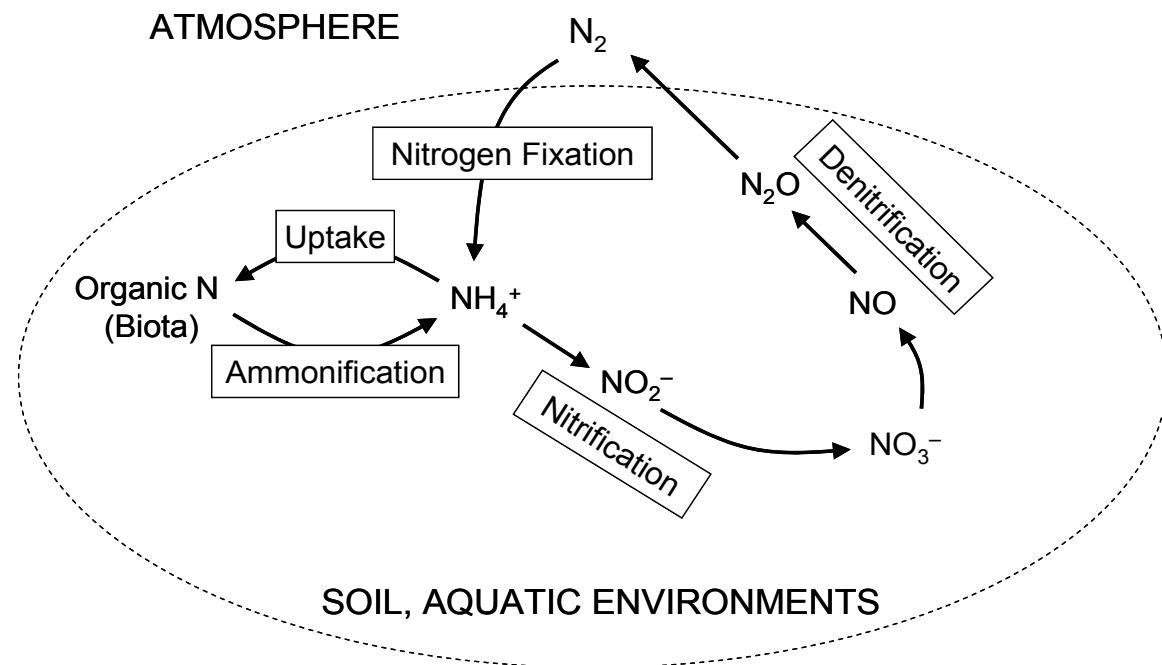
Ammonia is a key intermediate in the nitrogen cycle, a natural cycle that is coupled with other important biological cycles (i.e., the sulfur cycle and carbon cycle). An understanding of the role of ammonia in the nitrogen cycle, at least on a generalized level, is important in determining the environmental fate of ammonia. A simplified schematic of the microbial processes of the nitrogen cycle that involves ammonia can be found in Figure 6-2. Microorganisms perform four processes in the nitrogen cycle that result in

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Figure 6-1. Frequency of NPL Sites with Ammonia Contamination

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Figure 6-2. Simplified Schematic for the Microbial Processes of the Nitrogen Cycle



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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 N₂ and N₂O, 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 the organic N compounds present in these sources enter the water and are converted microbiologically to ammonia.

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 (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 H₂SO₄, HCl, HNO₃, 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.

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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).

6.2 RELEASES TO THE ENVIRONMENT

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

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commonly distributed to the environment during its intended use as a crop fertilizer. Release data generated for the Toxics Release Inventory (TRI) (see Table 6-1) 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 6-1 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

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Table 6-1. Releases to the Environment from Facilities that Produce, Process, or Use Ammonia^a

State ^c	Number of facilities	Reported amounts released in pounds per year ^b						Total on and off-site release
		Air ^d	Water	Under-ground injection	Land	Total on-site release ^e	Total off-site release ^f	
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

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State ^c	Number of facilities	Reported amounts released in pounds per year ^b						Total on and off-site release
		Air ^d	Water	Under-ground injection	Land	Total on-site release ^e	Total off-site release ^f	
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	0	119,829	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
Total	2,668	122,057,546	6,621,166	22,974,237	3,621,049	155,273,998	3,247,048	158,521,046

Source: TRI01 2003 (Data are from 2001)

^aThe 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.^bData in TRI are maximum amounts released by each facility.^cPost office state abbreviations are used.^dThe sum of fugitive and stack releases are included in releases to air by a given facility.^eThe sum of all releases of the chemical to air, land, water, and underground injection wells.^fTotal amount of chemical transferred off-site, including to publicly owned treatment works (POTW).

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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.

6.2.1 Air

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 NH₃ emissions originated from agricultural sources (Strogies and Kallweit 1996). In Russia, estimated NH₃ emissions from fertilizer applications and livestock sources accounted for 94% of the total NH₃ 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; Beyrouty 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 NH₃ 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 NH₃. Harper and Sharpe (1995) demonstrated almost no net atmospheric NH₃ flux in corn crops, due to their relatively similar emission and uptake rates of NH₃ over the growing season.

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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 NH₃ emissions, with domestic animal wastes contributing 42.3% of that. Recent studies, however, provided fairly uniform estimates of ~40% of global NH₃ 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).

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6.2.2 Water

The major point source of release to surface waters is from the effluents of waste water-treatment plants (Barica 1990; Crumpton and Isenhart 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 N₂-fixing cyanobacteria (also called blue-green algae) die and are decomposed.

6.2.3 Soil

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 N₂, and these organisms are widely dispersed throughout the soil (Atlas and

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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.

6.3 ENVIRONMENTAL FATE

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 NH₃ 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.

6.3.1 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

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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 NH₃ 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 H₂SO₄, HNO₃, or 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 ~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

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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 SO₂ 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 NH₄⁺ (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.

6.3.2 Transformation and Degradation

6.3.2.1 Air

In air, a dominant fate process for ammonia is the reaction with acid air pollutants. Formation of particulate NH₄⁺ compounds by reactions with HNO₃ and H₂SO₄ is rapid (Bouwman et al. 1997; Irwin

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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 1.6×10^{-13} cm³/molecule-sec, which translates to a calculated half-life of 100 days at a hydroxyl radical concentration of 5×10^5 molecules/cm³ (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 NH₃ emissions; where NH₃ emissions are lower, wet deposition of particulate NH₄⁺ predominates (Asman et al. 1998).

6.3.2.2 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, NO₂⁻ and NO₃⁻, 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, NH₄⁺. 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.

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6.3.2.3 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.

6.3.2.4 Other Media

No data exist for the transformation or degradation of ammonia in other media, apart from biological tissues. These transformations are discussed in more detail in Chapter 3.

6.4 LEVELS MONITORED OR ESTIMATED IN THE ENVIRONMENT

In discussing the concentration of ammonia monitored in the environment, it is important to consider both ammonia and its conjugate acid, the ammonium ion. Independent determination of these compounds cannot always be achieved. In an analysis of the literature, it is difficult to separate aqueous ammonia concentration from aqueous ammonia-ammonium concentrations unless the investigators made a special effort to determine the amount of un-ionized ammonia. In this section of the document, ammonia will refer to the ammonia and ammonium concentration, and un-ionized ammonia will refer specifically to the ammonia concentration.

In the atmosphere, ammonia can exist in its gaseous state, be dissolved in rain, the water of fog, or clouds, or be found as ammonium in particulates and aerosols. These species can be analyzed separately. For this reason, atmospheric ammonia concentrations reported in this document will refer to the concentration of gaseous ammonia, and not to the concentrations of ammonium compounds.

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6.4.1 Air

Ammonia has a worldwide atmospheric background concentration. Estimates of the average global ammonia concentration are approximately 0.6–3 ppb (Aneja et al. 1998; Crutzen 1983; Georgii and Gravenhorst 1977). Dawson and Farmer (1984) reported that the average concentration of ammonia in the southwestern United States is 0.9 ppb, which may be considered a representative background value because at the site of these measurements, the prevalent winds came from the Pacific Ocean and there were no known urban or agricultural ammonia sources nearby. Fangmeier et al. (1994) reported similar values in a review of effects of atmospheric ammonia on vegetation. Values measured at sea or at high altitude provided a background range of 0.06–1.0 ppb (n=9 reports). When atmospheric ammonia levels have been determined to be above background levels, the measurements can often be correlated with industrial, agricultural, or other activities that might occur in nearby areas (Fangmeier et al. 1994).

The concentrations of ammonia in the atmosphere vary across the United States, with concentrations being higher in the Midwest as compared to either the west or east coasts. Based on early data on the concentration of ammonia in rain, Lau and Charlson (1977) determined a trend for the atmospheric ammonia concentration across the United States. The estimation of atmospheric ammonia content increased progressively starting from the east coast to the mid-west and on to the western states. Upon reaching the Pacific coast, the atmospheric ammonia concentration decreases. It should be noted that the values obtained in this study (ppt levels over the eastern seaboard and pacific coasts, and low ppb levels in the midwest and western United States) tend to be lower than those determined by more recent experiments. For example, Aneja et al. (1998) measured concentrations of both NH_3 and NH_4^+ at Mount Mitchell (North Carolina) over 2 years; concentrations averaged 1–2 ppb. Fangmeier et al. (1994) provided atmospheric ammonia values derived from five studies conducted in the United States, with an average NH_3 concentration of 3.3 ppb. The general conclusion of Lau and Charlson (1977) however, appears valid, and is indicative of the trends found for the ammonia concentrations in the atmosphere. Atmospheric ammonia concentrations are expected to be highest near intense agricultural or livestock production areas because of ammonia emissions from fertilizer and animal excreta, respectively. Lower concentrations are generally expected in more industrialized areas because of diminished sources of agricultural emissions and the atmospheric reaction of ammonia with acidic compounds known to be produced in industrial emissions and automobile exhaust. Data summarized in Fangmeier et al. (1994) indicate that industrial regions may have significant ammonia concentrations, but these are orders of magnitude lower than concentrations in regions with some agricultural applications. Concentrations

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determined near industrial sources in Germany (10.3–39.1 ppb) were in the same order of magnitude as concentrations near manure heaps (89 ppb), but were three orders of magnitude lower than emissions near pigpens (4.7×10^4 ppb).

Ground-level ammonia concentrations taken at urban Hampton and rural Langley, Virginia, ranged from 0.2 to 4.0 and from 1.5 to 4.0 ppb, respectively, in the fall of 1979 (Harward et al. 1982). Ammonia concentrations obtained in December of 1979 on Long Island, New York, ranged from approximately 80 to 200 nmol/m³ (1.9–4.8 ppb) (Tanner 1982). The ground level ammonia concentrations in Claremont, Los Angeles, and Anaheim, California, were <25 ppb (Russell et al. 1988). In Riverside and Rubidoux, California, areas near dairy feedlots, the ground level ammonia concentrations were 37–132 ppb and approximately 10–100 ppb, respectively. Rural-area concentrations, however, in Massachusetts and New York were considerably lower (0.2–1.1 ppb) (Fangmeier et al. 1994).

The ambient concentrations of ammonia determined at Whiteface Mountain, New York, in 1982 ranged from approximately 0.3 to 5 ppb, with the hourly median and mean values both determined as 2.2 ppb (Kelly et al. 1984). Ammonia concentrations in rural Thurber, Nevada, ranged from approximately 0.5 to 2 ppb (Farmer and Dawson 1982). In the atmosphere over the world's oceans, ammonia concentrations ranged from approximately 0.28 to 5.6 ppb (Georgii and Gravenhorst 1977).

Several investigators have studied the seasonal variation of ammonia concentrations in the atmosphere. In Hampton, Virginia, the ground level ammonia concentrations during the spring and summer were 10 and 1 ppb, respectively (Levine et al. 1980). The difference in concentration may have been due to volatilization of ammonia resulting from springtime application of fertilizer in nearby agricultural areas. In Warren, Michigan, the average ammonia concentrations measured during the summer, fall, winter, and spring were 0.85, 0.37, 0.10, and 0.16 ppb, respectively. The difference in concentrations was attributed to fluctuations in emissions from livestock excreta, since natural ammonia emissions are much higher in the summer than in the winter (Cadle 1985; NRC 1979). Additionally, in colder weather, microbial activity would be expected to decrease, and thus, ammonia emissions from the decay of organic matter would also be expected to decrease. Ammonia emissions from animal excretions also fluctuate with the time of day (Beauchamp et al. 1982; Brunke et al. 1988).

The concentration of ammonia in the atmosphere decreases with altitude. Levine et al. (1980) found that an ammonia concentration of 10 ppb measured at ground level decreased to a concentration of 1.5–3 ppb at a height of 10 km. In a historical modeling study on the European production of ammonia, levels based

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on ammonia release from livestock, fertilizer production and application, human and domestic animals, and sewage sludge resulted in average atmospheric ammonia concentrations ranging from 0.6 to 1.4 ppb for 1970 and from 0.7 to 5.6 ppb for 1980. The greatest increase occurred between 1950 and 1980, when synthetic fertilizer application and high nitrogen content feed grains were widely used (Asman and Drukker 1988). The ammonia concentration over a field during the application of gaseous ammonia fertilizer was as high as 300 ppb (Denmead et al. 1982). Over cattle feedlots, atmospheric ammonia concentrations have been measured at 520–2,160 ppb (Hutchinson et al. 1982).

6.4.2 Water

The concentration of ammonia in the Ochlocknee River at the head of Ochlocknee Bay, Florida, ranged from approximately 31 to 43 ppb, and concentrations of approximately 8.5 to 26 ppb were determined at the mouth of the bay (Seitzinger 1987). The concentration determined in the Ochlocknee River is consistent with levels reported for unpolluted tropical rivers (Meybeck 1982). Typical ammonia levels in the South Skunk River, Iowa, upstream from a municipal sewage-treatment facility were <1 ppm (Crumpton and Isenhart 1988). Downstream of the facility, ammonia levels peaked at approximately 16 mg/L (16 ppm), with levels of un-ionized ammonia ranging from <1.0 to 2.2 ppm. The levels of undissociated ammonia were directly related to pH fluctuations in the river. The authors did not discuss why the upstream concentration was so high. In the same study, it was noted that ammonium and un-ionized ammonia concentrations fluctuated in a diurnal pattern in the river, with peaks in ammonia (approximately 1 mg/L) occurring around noon, and low concentrations (0.5 mg/L) occurring usually after midnight (Crumpton and Isenhart 1988). The mean ammonia concentration in three Illinois rivers ranged from 0.28 mg/L (0.28 ppm) to 6.08 mg/L (6.08 ppm). The lower values were associated with agricultural sampling points and the higher values were associated with urban sampling points (Wilkin and Flemal 1980).

The ammonia concentration measured in Hamilton Harbour, Ontario, Canada was typically 0.1–3 mg/L (0.1–3 ppm) in the early 1980s. This body of water is used for water transportation (e.g., boat and barge traffic), as a source for industrial cooling water, and as a receptor for waste water disposal (Snodgrass and Ng 1985). Measurements made a few years later (1987–1988), in contrast, showed much lower concentrations. Measured concentrations, however, were still greater than the International Joint Commission objective of 20 : g/L (20 ppb) for more than half the year, and concentrations often exceeded the chronic toxicity threshold of 300 : g/L (300 ppb) (Barica 1990). This work reported that ammonia

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loadings into Hamilton Harbor had decreased over the late 1970s and 1980s, and the measured concentrations may reflect that change.

Some representative data regarding the concentration of ammonia in groundwater indicate that natural concentrations are generally low, but that agricultural practices can, at times, lead to higher levels. Low levels of ammonia have been found in groundwater wells under cattle and poultry feed lots, and in shallow wells. Wells 3–6 m deep showed little variation in ammonia concentration over a 3-year period where varying amounts of chicken manure were spread over agricultural plots, except when excessive amounts (54–179 metric ton/ha) were applied (Liebhardt et al. 1979). Groundwater levels of ammonia were also determined in an area in Idaho that had previously been noted as having high nitrogenous compound concentrations in the water. In this study, ammonium concentrations varied from 2.5 ppb in a municipal drinking water well to 3.25 ppm in a deep, private well (Wicherski 2000). Shallow wells in North Carolina had typical ammonia concentrations of 0.1–1 ppm, which were independent of land use, plant type, and amount of fertilization (Gilliam et al. 1974). Water samples from wells on four schoolyards in Michigan that used septic tank sewage systems had ammonia concentrations ranging from 0 to 733 ppb (Rajagopal 1978). In the Netherlands, the ammonium concentration detected in sample cups buried 1.2 m in the ground near forests ranged from 0 to 2.3 ppm (Krajenbrink et al. 1988), but no ammonia was detected in deeper wells (12.6 meters) analyzed in this study. The high adsorptivity of ammonium to soil and the rapid conversion of ammonia to nitrate by microbial action are both consistent with the usual finding of very low ammonia concentrations in groundwater.

Ammonia was measured in rain and snow samples from three sites in northern Michigan in 1978–1979. Concentrations ranged from 23.8 to 3,500 ppb, with mean values for each site of 816, 572, and 632 ppb, respectively. Concentrations were generally greatest in the spring and fall and were lowest during the winter (Munger 1982). Ammonia concentrations in bulk precipitation obtained in the Netherlands had median values ranging from 1.33 ppm in ocean areas to 5.09 ppm in bodies of water near heavily agricultural areas (Schuurkes et al. 1988).

Ammonia concentrations in the influent to sewage-treatment plants, and thus the effluent from sewer systems, typically range from 10 to 20 ppm (Englande et al. 1978; Hauser 1984; U.S. Army Corps of Engineers 1980). Waste water-treatment plant effluent is one of the few types of point sources of ammonia emissions to surface water. In a study of several waste water-treatment plants, eight of nine plants exceeded the guideline ammonia concentration (0.5 mg/L), with measured median values at these sites ranging from 0.08 to 15 mg/L (0.08–15 ppm) (Englande et al. 1978).

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No data were located in the available literature regarding ammonia concentrations in drinking water. This may be attributed to the rapid reaction between ammonia (and ammonium) and the chlorinating agents used in water treatment plants (Morris 1978).

6.4.3 Sediment and Soil

A 4-year study on ammonia levels in the soil (0–10 cm deep) of an open field (samples obtained in early May of each year) showed that ammonia concentrations ranged from 1 to 5 ppm (Beauchamp et al. 1982). The day after application of a slurry of liquid cow manure, the soil concentration ranged from 2 to 3,349 ppm. Five days after application, the concentration of ammonium ranged from 2 to 848 ppm. The greatest ammonia concentration was in the uppermost 4 cm of soil.

Ammonia was found at 137 of 1,647 hazardous waste sites on the NPL of highest priority sites for possible remedial action (HazDat 2004).

6.4.4 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).

6.5 GENERAL POPULATION AND OCCUPATIONAL EXPOSURE

The most probable routes by which the general population is exposed to ammonia are by the inhalation of ammonia that has volatilized from common household cleaning products and through dermal contact during the use of these products. Inhalation exposure to ammonia by some members of the rural population may occur for those who are near agricultural areas during the fertilizer-application period, those near animal feedlots or confinement areas, and those who apply anhydrous ammonia or ammonia-producing fertilizers to fields. There is also the possibility for exposure to ammonia via water and food

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ingestion. If untreated surface water is ingested, the average uptake would be 0.36 mg/day (assuming an ammonia concentration in untreated water of 0.18 mg/L and a consumption of 2 L/day) (WHO 1986). Food ingestion could lead to an exposure to ammonia, primarily from the use of various ammonium salts as stabilizers; the estimated exposure from these food additives is 18 mg/day (WHO 1986).

In the National Occupational Hazard Survey (NOHS) of 1972–1974, it was statistically estimated that 2,524,678 workers are exposed to ammonia in the United States (RTECS 1988). According to the National Occupational Exposure Survey (NOES), in 1989, 681,780 workers (231,208 of whom were female) were estimated to be exposed to ammonia (NOES 1989). A correlation of data from the EPA Air Toxics Emission Inventory with industrial source codes (SIC codes) shows that volatile emissions of ammonia are associated with 212 different industrial classifications (EPA 1987b).

Workers in swine- and poultry-confinement buildings may be exposed to elevated levels of ammonia (Attwood et al. 1987; Crook et al. 1991; Donham and Popendorf 1985; Jones et al. 1984; Leonard et al. 1984; Liao and Bundy 1995). Average ammonia concentrations in the air of these buildings depend on numerous factors; representative values ranged from 0.28 to 42.2 ppm (280–42,200 ppb) (Attwood et al. 1987; Fangmeier et al. 1994), but in buildings with slow ventilation rates, concentrations exceeded 80 ppm (Liao and Bundy 1995). It should be noted that workers in these buildings may also be exposed to other materials in addition to ammonia, including particulate material (small dessicated manure particles), endotoxin, and others which may lead to combined exposures.

Ammonia levels in air at an ammonium phosphate fertilizer-production plant ranged from 3 to 75 ppm (3,000–75,000 ppb) (NIOSH 1987). In a Finnish plywood factory, short-term ammonia concentrations during the mixing of urea-formaldehyde glue were 50–70 ppm (50,000–70,000 ppb) (Kauppinen 1986). Ammonia concentrations at 42 facilities using a blue-line printing system were 1–40 ppm (1,000–40,000 ppb) (Tuskes et al. 1988). Workers at coal-gasification units may be exposed occupationally to ammonia (Jin et al. 1999; Van Hoesen et al. 1984). Workers at ammonia transportation and storage facilities can be exposed to ammonia during the transfer between facilities, from the venting of built-up pressure in tanks, and during leaks or spills.

Farmers can be exposed to ammonia when applying fertilizer. The ammonia concentration over a field during the application of gaseous anhydrous ammonia fertilizer was as high as 213 $\mu\text{g}/\text{m}^3$ (300 ppb) (Denmead et al. 1982). Workers at cattle production facilities (e.g., feedlots, farms) and those who work under conditions where volatilization from animal excreta would be enhanced may be occupationally

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exposed to ammonia. Over cattle feedlots, atmospheric ammonia concentrations have been measured at 373–1,540 µg/m³ (520–2,160 ppb) (Hutchinson et al. 1982). Exposure to ammonia can occur by inhalation in the liquid manure-storage facilities of swine-confinement buildings. Ambient air levels have been measured at up to 50 ppm (50,000 ppb) in these facilities (Donham et al. 1982).

6.6 EXPOSURES OF CHILDREN

This section focuses on exposures from conception to maturity at 18 years in humans. Differences from adults in susceptibility to hazardous substances are discussed in Section 3.7 Children's Susceptibility.

Children are not small adults. A child's exposure may differ from an adult's exposure in many ways. Children drink more fluids, eat more food, breathe more air per kilogram of body weight, and have a larger skin surface in proportion to their body volume. A child's diet often differs from that of adults. The developing human's source of nutrition changes with age: from placental nourishment to breast milk or formula to the diet of older children who eat more of certain types of foods than adults. A child's behavior and lifestyle also influence exposure. Children crawl on the floor, put things in their mouths, sometimes eat inappropriate things (such as dirt or paint chips), and spend more time outdoors. Children also are closer to the ground, and they do not use the judgment of adults to avoid hazards (NRC 1993).

Three recent studies focused on the exposure of children to ammonia or the effects that exposure may have on children, all of which noted little effect on the children's health (Gomzi 1999; Gomzi and Saric 1997; Suh et al. 1992). One of the studies focused on the respiratory effects among people living near a fertilizer plant, another study investigated the effects of living in an urban vs. rural area, and a third study investigated the general effects of acid aerosols on children living in a semi-rural area. In general, these studies noted that exposure to low levels of ammonia had very little impact on the health of the children. The studies did find that other factors, such as parental smoking, had more profound effects on the children's respiratory health.

One study compared the effects of living near a fertilizer factory on the respiratory health of 8–9-year-old children (Gomzi and Saric 1997). The study found that the air quality near a fertilizer plant was within acceptable limits for most of the measurement period, with only a few fluctuations beyond acceptable limits. While these fluctuations correlated somewhat with health parameters measured on children living nearby, the rate of respiratory disease was more influenced by indoor air pollution sources than by

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outdoor sources. No significant effect was observed due to exposure to ammonia at the concentrations seen in the study.

A second study of 223 children (8–10 years old) living in Croatia found that indoor air quality had a slightly greater effect on respiratory health in urban areas compared to those living in rural areas (Gomzi 1999). The differences, however, were not significant. The study found no influence of ammonia on the children's respiratory health, but did find that parental smoking had a significant negative impact on their respiratory health.

A third study evaluated SO_4^{2-} and H^+ exposure to 24 children (ages were not provided) living in Uniontown, Pennsylvania (Suh et al. 1992). This study did not focus on ammonia exposure *per se*, but on other airborne contaminant concentrations in aerosols found outdoors, indoors, and by personal monitors. It sought to determine how personal exposures to these aerosols correlated with indoor and outdoor concentrations. Ammonia concentrations were measured in order to assess their potential for neutralizing H^+ found in aerosols. Ammonia concentrations were found to be highest near the children (detected by the personal monitors), followed by indoor concentrations, and were minimal outdoors. It was proposed that a large proportion of the H^+ found in indoor aerosols are neutralized by NH_3 , and would thus lower the children's exposure to acid aerosols. The authors noted that more research is needed to fully model the influence of factors, including NH_3 , on indoor acid aerosol exposure.

6.7 POPULATIONS WITH POTENTIALLY HIGH EXPOSURES

Workers in industries that commonly use ammonia, especially if there are no adequate safety and/or venting systems, may be at risk for potentially high exposure to ammonia. Examples of these might include farm workers who are employed in inadequately-ventilated, enclosed spaces with high concentrations of animals. Other examples include workers who process ammonia or transfer it from shipping containers to pipelines. The general population is at risk to high levels of exposure if cleaning products containing concentrated solutions of ammonia are used in small, enclosed, or unventilated rooms.

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6.8 ADEQUACY OF THE DATABASE

Section 104(i)(5) of CERCLA, as amended, directs the Administrator of ATSDR (in consultation with the Administrator of EPA and agencies and programs of the Public Health Service) to assess whether adequate information on the health effects of ammonia is available. Where adequate information is not available, ATSDR, in conjunction with the National Toxicology Program (NTP), is required to assure the initiation of a program of research designed to determine the health effects (and techniques for developing methods to determine such health effects) of ammonia.

The following categories of possible data needs have been identified by a joint team of scientists from ATSDR, NTP, and EPA. They are defined as substance-specific informational needs that if met would reduce the uncertainties of human health assessment. This definition should not be interpreted to mean that all data needs discussed in this section must be filled. In the future, the identified data needs will be evaluated and prioritized, and a substance-specific research agenda will be proposed.

6.8.1 Identification of Data Needs

Physical and Chemical Properties. The physical and chemical properties of ammonia have all been well documented, and there do not appear to be any data needs in this area.

Production, Import/Export, Use, Release, and Disposal. The large amounts of ammonia produced in nature and in household products indicate that the risk for human exposure to ammonia exists. Data regarding the commercial production, disposal, and use of ammonia are well understood. Data regarding the production of ammonia by natural organisms, and its global and regional concentrations are not as well understood, nor are the influences of different process strategies on livestock ammonia emissions. This information would be useful in determining the contribution of anthropogenic ammonia to the global budget of this compound, which would help in determining the human influence on the global cycle.

According to the Emergency Planning and Community Right-to-Know Act of 1986 (EPCRA), (§313), (Pub. L. 99-499, Title III, 9313), industries are required to submit release information to the EPA. The TRI contains release information for 2001. This database is be updated yearly and provides a more reliable estimate of industrial production and emission.

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Environmental Fate. Since ammonia is a key intermediate in the nitrogen cycle, the environmental fate of ammonia should be interpreted in terms of its involvement in this cycle. Information available on the environmental fate of ammonia is sufficient to define the basic trends, and data are available regarding the direction of changes in these trends resulting from changes in the key variables. There are many subtle facets of the fate of ammonia in the environment that depend on nature and its cycles. Thus, accurately predicting the environmental fate of ammonia is not possible with our present knowledge.

An understanding of the environmental fate of ammonia is important when considering that human contribution to the global ammonia budget has grown over the years. A complete understanding of the environmental fate of ammonia will then allow an understanding of any changes that might occur from the role of ammonia in the nitrogen cycle. Since all living organisms depend on the nitrogen cycle, either directly or indirectly, this information would allow any decisions concerning ammonia to be made in an informed and prudent manner.

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, Analytical Methods). 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

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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.

6.8.2 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 below and in Table 6-2. 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.

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Table 6-2. Ongoing Studies on Environmental Fate and the Potential for Human Exposure to Ammonia

Investigator	Affiliation	Research 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

6. POTENTIAL FOR HUMAN EXPOSURE

Several studies are being conducted to lessen exposures to ammonia. Researchers at the University of Kentucky are investigating methods to reduce emissions of ammonia from poultry houses by improving manure handling. In a different approach, researchers at the University of Idaho are investigating changes in animal diet as a means to improve the abilities of livestock to more completely incorporate ruminal ammonia nitrogen into milk and protein. If successful, both will result in lower exposures to excreted ammonia. Furthermore, both approaches will lead to more knowledge regarding the efficient transformation of ammonia into useful products, either compostable manure or food products.

A considerable number of studies are being conducted to provide better determinations of atmospheric transport and deposition of ammonia, either on a local scale or a global scale, and for reducing ammonia effluents from animal waste. The U.S. Department of Agriculture (USDA) at Watkinsville and Athens, Georgia, in conjunction with the University of Tennessee at Knoxville, is investigating approaches to reduce ammonia emissions from poultry, dairy, and swine facilities, with the objective being to reduce short- and long-term ammonia losses that affect indoor and outdoor air quality. The USDA in Fayetteville, Arkansas is testing different approaches to reduce ammonia emissions from poultry, swine, and dairy facilities via evaluation of the efficacy of alum treatments. Other research efforts being conducted by the USDA include the evaluation of the best use and application practices of animal manures that contain ammonia to reduce emissions and favor nutrient transfer to crop soils. Mississippi State University researchers are evaluating the quality of poultry effluents and swine litter for use as manure-based fertilizers for crops, wherein the efficiency of manure nutrient (including ammonia) transfer to the crop soils is being evaluated. Research is also being conducted at Mississippi State University to evaluate the use of cellulosic materials (i.e., kenaf) to decrease ammonia and odor emissions from poultry waste. Kenaf has several attractive characteristics as a biosorbent for ammonia, and is therefore being evaluated for the removal of odors and ammonia from waste streams. In another study being conducted at Mississippi State University, five treatments (copper chlorophyllin, chitosan, activated carbon, kenaf, and paper mill sludge) are being compared for their effects on reducing emissions from poultry litter. The findings indicate that the materials have different efficiencies for reducing overall odor emissions, but no report has been provided about their specific effects on ammonia emissions.