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Ammonia exposure and hazard assessment for selected household cleaning product uses

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There is scant information pertaining to airborne ammonia exposures from either spills or common household uses of ammonia-containing floor and tile cleaners or from spray-on glass cleaners. We assessed instantaneous and event-specific time-weighted average (TWA) exposures to airborne ammonia during spills and use (per label directions) of a household floor and tile cleaner and two spray-on window cleaners. Airborne ammonia levels measured at breathing zone height (BZH) above the spilled floor and tile cleaner product reached 500 p.p.m. within 5 min, while levels for spilled window cleaner were below 8 p.p.m. TWA exposures were assessed while tile walls and floors were cleaned in three different bathrooms of a residence, and during use of a spray-on glass cleaner while washing several large windows in an office setting. NIOSH Method 6015 was utilized with concurrent field measurements every 60 s using a Drager PAC III monitor with an electrochemical cell detector. Peak ammonia levels ranged from 16 to 28 p.p.m. and short-term TWA concentrations ranged from 9.4 to 13 p.p.m. during mixing (0.1% ammonia) and cleaning tiles in the three bathrooms. Ammonia exposures while using spray-on window cleaner were over 10-fold lower (TWA = 0.65 p.p.m.). Use of the floor and tile cleaner mixed at 0.2% ammonia led to peak airborne ammonia levels within 3–5 min at 36–90 p.p.m., and use of full strength cleaner (3% ammonia) led to peak ammonia levels of 125 to >200 p.p.m. within 2–3 min. Spillage or intentional use of the full strength floor and tile cleaner led to airborne ammonia concentrations that exceed occupational short-term exposure limits, while spillage or use of the spray-on window cleaner did not approach potentially hazardous airborne ammonia levels and likely represents a minimal inhalation health hazard. We conclude that routine household uses of ammonia are unlikely to produce significant exposures when using standard cleaning solutions (0.1–0.2%), but spillage or use of concentrated ammonia solutions (e.g., 3%) in poorly ventilated areas can lead to potentially hazardous airborne ammonia exposures.

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Introduction

Ammonia is a widely used hazardous chemical with many potential applications in agriculture, industry, and commercial products, including various household cleaning products. The most likely source for ammonia exposure in the general population is from the use of household cleaners containing ammonia or ammonium salts (ATSDR, 2002). Ammonium hydroxide (“ammonia”) is the primary active agent for cleaning and disinfecting nonporous surfaces in various domestic, commercial, and “industrial strength” cleaning products. Its widespread use and the popular knowledge of ammonia as a strong cleaning and disinfecting agent leads to a strong potential for use of relatively concentrated forms by individuals who may not be fully informed about the potentially serious inhalation health hazards associated with improper uses of this chemical. Nazaroff and Weschler (2004) reviewed the hazard potential of a variety of cleaning products, including certain ammonia-containing cleaners.

As explained later in detail (in the “Review of Dose–Response Considerations” section), ammonia is a well-recognized corrosive agent and sensory irritant with relatively good warning properties due to its pungent odor and the irritation effects of airborne exposure, which promote avoidance of continued exposure. Although there are well-known serious health consequences from oral and dermal exposure to concentrated ammonia solutions (ATSDR, 2002), the focus of the present study is on inhalation exposures and associated health risks. Acute inhalation exposures are of particular importance because ammonia dose–response relationships demonstrate a relatively steep dose–response that is highly dependent on “concentration times duration,” that is, brief, high exposures are typically most hazardous (NAS, 1987; NIOSH, 1997; AIHA, 2001; ATSDR, 2002). Moreover, many individual-specific factors such as age, smoking history, and underlying chronic lung

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diseases can influence the severity and permanence of ammonia-induced lung damage or functional deficits (WHO, 1986; NAS, 1987; ATSDR, 2002).

The purpose of the current study was to examine in a quantitative manner the nature and extent of ammonia exposure during household use and spills of selected ammonia-containing cleaning products. Two types of cleaning products were examined: (1) a floor and tile cleaning concentrate solution stated to contain 5% ammonium hydroxide, and (2) a spray-on glass cleaning solution stated to contain 1–3% ammonium hydroxide. Instantaneous and TWA airborne exposures to these products were simulated during normal use and accidental spill scenarios. We also provide an overview of the dose–response considerations regarding ammonia inhalation exposures and a product-specific hazard assessment to place our exposure assessment findings in perspective with the available human studies on health hazards of inhaled ammonia.

Methods

Products Assessed

The household ammonia-containing cleaners that were evaluated in the current study include a typical "store brand" ammonia concentrate (5% ammonia by volume per the product label) sold for general use as a floor and tile cleaner, as well as ready-to-use formulas of a "name brand" glass cleaner (1% and 3% ammonium hydroxide per the material safety data sheet) and a "store brand" glass cleaner (ammonia content not stated). There are many similar name brand and store brand products to these offered at grocery stores and other stores throughout the United States. The floor and tile cleaner product was purchased in a 64-ounce volume in a plastic container with a screw cap top. The window cleaner products were purchased in 32 ounce plastic bottles with a mechanical pump sprayer.

Product Ammonia Content Determination

Each of the three products was evaluated for pH and total dissolved nitrogen content at a commercial laboratory (Galbraith Laboratories, Knoxville, TN, USA) certified for commercial products analysis by Good Manufacturing Practices (GMP) certification, as well as Good Laboratory Practices (GLP) and USEPA laboratory certifications. The pH was determined by using an Accumet pH Meter, Model 25. Dissolved ammonia concentrations were assessed by determining the dissolved nitrogen content in each solution using the Total Kjeldahl Nitrogen method (Bradstrut, 1965). Duplicate samples were evaluated for two of the three products assayed. Since the solution pH was approximately 11 in each product, essentially all of the dissolved nitrogen was likely to be in the form of ammonia. Dissolved ammonia concentrations were calculated by multiplying the dissolved nitrogen results (mg/l) by 1.43 to correct for the molecular weight difference between ammonia and nitrogen ($10/7 = 1.43$).

Spill Exposure Studies

A pilot study was conducted to examine exposures created by a simulated accidental spill wherein the newly opened product container was tipped over and allowed to spill out on a level surface (within a bathtub with the drain plugged). This procedure caused approximately half of the container to spill out, and the volume spilled for each container was assessed as the average of three trial spill simulations using the same containers filled with the same volume of water and measuring the amount remaining in the container. Drager colorimetric tubes (Drager-Rohrchen, no. 8101941, Lubeck, Germany) were utilized in the pilot study to measure airborne concentrations between 5 and 100 p.p.m. Measurements were taken at 2 ft above the spilled liquid and at adult breathing zone height (BZH) (5 ft) at selected time periods after spilling a known amount of the cleaner product. The bathtub enclosure of bathroom 3 was utilized with the tub drain closed. During the spill study in this small bathroom (about 320 ft^3), the bathroom fan (30 cubic feet per minute, cfm) was operating, the entry door was open (no windows), and the shower enclosure sliding glass door was kept open about 2 ft on one side for access. The shower door structure did not entirely enclose the bathtub area; there was 18 in of open space vertically between the top of the door structure and the ceiling above the bathtub. Ambient indoor temperature was approximately 67°F. The "name brand" window cleaner spill was studied first, then the floor and tile cleaner spill was studied approximately 2 h later. Drager tube measurements prior to each spill event indicated no detectable airborne ammonia (<1 p.p.m.).

The pilot spill study with the floor and tile cleaner was repeated two additional times because most of the measurements in the pilot study had exceeded the calibration limit (5–100 p.p.m.) of the Drager tubes utilized. In subsequent experiments, a higher capacity (50–700 p.p.m.) colorimetric tube (Drager-Rohrchen, no. 80020501, Lubeck, Germany) was utilized and measurements were made primarily at 5 ft to simulate the BZH of a typical adult. The container size and amount spilled were identical to the pilot study but were assessed in a different residence location. A small bathroom (560 ft^3) with standard bathtub enclosure was utilized, although there was no ventilation fan and a single window in the bathroom was opened at 15 min after each spill. Ambient indoor temperature was approximately 65°F. All measurements were made within the enclosure at 2 or 5 ft above the spilled liquid in the bathtub. All samples taken at 2 ft above the liquid were collected to examine the ammonia vapor distribution with distance above the spilled liquid, not to simulate any specific personal exposure situation.

Household Tile and Window Cleaning Exposure Studies

Personal exposures to ammonia were assessed for each product under use conditions as directed on the labels. Mixing of the floor and tile cleaner involved a standing adult pouring the concentrate into a measuring cup placed on a countertop (about 30 in) to dispense one cup (8 ounces) of the cleaner immediately into a cleaning bucket (on the floor) containing either 1 or 2 gallons of hot water (approximately 105°F). The window cleaner (no mixing needed) was sprayed directly onto the windows liberally, such that larger droplets tended to condense and run down the windows over most of the surface area being cleaned.

We assessed instantaneous and event-specific TWA exposures to airborne ammonia for a person performing household cleaning with the floor and tile cleaner product in three tiled bathrooms of one house. Personal samples and area monitoring were conducted during mixing and cleaning as described below. Exposure monitoring was conducted during mixing and use (cleaning with a soaked sponge), with less than 2 min to switch equipment between each of the bathrooms. All tiled and glass surfaces in each bathroom were washed with the soaked sponge using the floor and tile cleaner. Each of the bathrooms contained a standard (30 cfm) exhaust fan that was in operation throughout the study, and the entry doors (all three rooms), shower/bathtub enclosure doors (all three rooms), and window (only for bathroom 2) were kept open during cleaning activities. Bathroom 1 was a small bathroom (approximately 280 ft^3) with a tiled floor, 24 in tiled vanity with 2 × 3 foot mirror and fully tiled shower enclosure with glass door. Bathroom 2 was a large master bathroom (approximately 720 ft^3) with a tiled floor, large garden tub with tile surround up to 4 ft, a separate fully tiled shower enclosure with glass door, and a 6 ft double vanity with a 4 × 6 ft wall mirror. Bathroom 3 was another smaller bathroom (approximately 320 ft^3) with a tiled floor, 20 in pedestal sink with 1.5 × 3 ft mirror and standard bathtub with a sliding glass enclosure that was tiled from tub to ceiling. The tub in bathroom 3 was also used for the pilot spill scenario exposure study described above.

Airborne ammonia concentration *versus* time profiles were also assessed for a variety of cleaning scenarios with diluted or full strength (concentrate) floor and tile cleaner in a separate residence. This included cleaning and scrubbing the tile floor in two bathrooms and a den area, as well as use of poured concentrate on countertops in the kitchen and bathrooms, and use of concentrate inside the bathtub enclosures. The volume of concentrate used in each cleaning scenario was approximately 4 tablespoons or capfuls (1 capful = 1 tablespoon), where the person cleaning quickly measured out 4 capfuls, poured it on the countertop and spread it evenly using dry paper towels. Bathroom 4 was approximately 560 ft^3 with a 70 ft^2 tiled floor, tiled double vanity (12 ft^2), and tiled bathtub enclosure with glass entry door that had an 18 in vertical space above the glass enclosure. Bathroom 5 was approximately 470 ft^3 with a 59 ft^2 tiled floor, tiled double vanity (10 ft^2), and tiled bathtub with glass entry door with an 18 in vertical space above the glass enclosure. The bathroom doors and bathtub enclosure doors were left open during each cleaning study. The den was a tiled area within a larger open area of the house with a volume of approximately 4600 ft^3. The kitchen area had approximately 21 ft^2 of countertop area that was cleaned within a 1600 ft^3 volume that was open on one side to the den area. In this residence, there was no active ventilation with outdoor air from windows, exterior doors, fans, or air conditioning devices until the cleaning steps were completed, as noted in the figures.

We also assessed exposures during use of the "name brand" spray-on glass cleaner, while washing several large windows in an office setting. Standard office building air conditioning was operating during the study. Seven large panel windows (approximately 5 × 5 ft) were washed during the study, one panel at a time, using paper towels to wipe and dry each panel. Four of the window panels were contained in one large office (approximately 2600 ft^3) and the remaining three panels were contained in an adjacent office (approximately 1600 ft^3). Similar window cleaning procedures were completed in a different office building using the "brand name" window cleaner and separately using a "store brand" window cleaner using the PAC-III monitor only. The volume of product used during spraying of similar square footage of window space was determined by weighing the containers before and after the cleaning for three iterations.

Airborne Ammonia Measurement Methods

For the tile and window cleaning studies, two different measurement methods were utilized: NIOSH Method 6015 and the Drager PAC(III) field monitor. The first is a laboratory-based method that involved collection of air at BZH using a calibrated, battery-operated pump (SKC Universal, model 224-PCXR4, Valley View, PA, USA) that pulled air through a sorbent tube (SKC item no. 226-10-06, 6 × 60 mm size, 2-secction, 100/200 mg silica gel). Each tube was labeled and sent with chain of custody records to an American Industrial Hygiene Association (AIHA) certified laboratory (DataChem Laboratories, Salt Lake City, UT, USA) that extracted the sample and measured ammonia levels in accordance with NIOSH Method 6015. In the first set of bathroom tile cleaning studies (bathrooms 1, 2, and 3), the person performing the cleaning activities (MJF) had one BZH monitor on his collar/lapel (in addition to the PAC-III monitor) while cleaning all three bathrooms. Concurrent area samples located in the center of each bathroom at BZH were collected only during the cleaning activities in that room, and were analyzed by NIOSH Method 6015. In the second series of measurements in a separate residence (bathrooms 4 and 5, den and kitchen), the PAC-III monitor was again worn on the collar or lapel of the person performing the mixing and cleaning tasks, but no area samples were collected.

The Drager PAC III monitor was equipped with an electrochemical cell detector (DragerSensor XS EC NH3-68 09 145, Drager, Germany) that was pre- and post-calibrated for ammonia. The PAC(III) monitor samples a continuous stream of air and records a measurement every 60 s. The monitor was calibrated to measure airborne ammonia levels up to 200 p.p.m. with a reliable detection limit of 3 p.p.m. identified by the manufacturer. Instrument calibration was checked by the industrial hygiene supply firm before and after the two series of measurements and no notable deviations were identified (< 5% variance between the pre- and post-test calibration check, data not shown).

Results

Cleaner Product Ammonia Content

Table 1 provides a summary of the measurements for pH and ammonia content of the three cleaner products examined in these studies. The floor and tile cleaner, which on the label and material safety data sheet (MSDS) was said to be a 5% ammonia solution, was found to contain about 3% ammonia (wt/vol). The "name brand" glass cleaner, said to contain between 1% and 3% ammonia on the 2001 MSDS, was found to contain only about 0.1% ammonia. A 2004 MSDS for the same name brand product did not indicate the ammonia content. A similar glass cleaner that was a "store brand" product was found to contain approximately 0.05% ammonia and also did not list the ammonia content on their 2004 MSDS. Two of the three samples were analyzed in duplicate assays and found to be in close agreement (<5% variance, see footnote of Table 1). The pH of all three tested products was quite basic, with both glass cleaners at around pH 10.9 and the floor and tile cleaner at pH 11.7, indicating that essentially all of the ammonia in solution was likely in the form of dissolved NH_3, not ammonium ion (NH_4^+). Testing of the diluted floor and tile cleaner indicated similar basic pH (approx. pH 10 with litmus paper) to that shown for the ready-to-use glass cleaners in Table 1 (data not shown).

Table 1. Measurement of dissolved ammonia content in tested cleaner products.

Product	Stated ammonia content	Dissolved ammonia[a] and percent wt/vol	Measured pH[b]
Floor and tile cleaner, full strength	Up to 5% ammonia per MSDS	28,700 mg/l[c] 2.9%	11.67
Name brand glass cleaner, ready-to-use	Not stated on current MSDS[d]	950 mg/l 0.095%	10.86
Store brand glass cleaner, ready-to-use	Not stated on current MSDS	530 mg/l[e] 0.053%	10.88

[a] Total Kjeldahl Nitrogen method (Bradstrut, 1965) with adjustment from N to NH_3 (1.43).
[b] pH measurements were made using an Accumet pH Meter, Model 25.
[c] Average of the original and duplicate samples: 27860 and 29030 mg/l.
[d] Prior MSDS indicated up to 1 to 3% ammonium hydroxide content.
[e] Average of the original and duplicate samples: 526 and 531 mg/l.

Spill Exposure Studies

Table 2 provides a summary of airborne ammonia concentrations measured in the tub enclosure of bathroom 3 following spillage of about half of each container of the floor and tile cleaner and the spray-on window cleaner; weights before and after the simulated spills corresponded with averaged spilled volumes of 33.1. and 17.3 ounces, respectively (three trials each container, data not shown).

Table 2. Airborne ammonia concentrations above spilled cleaner products in a bathtub with glass enclosure.

Product/volume spilled	Time (min)	Ammonia concentration (p.p.m.)	
		At 2 ft	At 5 ft
Pilot study			
Floor and tile cleaner, 32 oz spilled	2	>100	90
	5	>100	>100
	10	>100	>100
Name brand spray-on window cleaner, 16 oz spilled	2	6	2
	5	8	4
	10	8	4
Repeated trials (Location 2)			
Floor and tile cleaner, 32 oz spilled, trial #1	2		150
	5		450
	10	550	550
	15		550
	20		300
	30		100
Floor and tile cleaner, 32 oz spilled, trial #2	2		200
	5		550
	10	550	500
	15		550
	20		250
	30		120

Ammonia concentrations determined using Draeger colorimetric tubes at specified height above the liquid spilled in a bathtub within a sliding glass door enclosure with one side open to bathroom 3 and the bathroom door open. Samples taken prior to each spill event showed nondetect (<1 p.p.m.). In location 2 (bathroom 4), a window was left open during the spill studies.

Ammonia concentrations in the pilot study frequently exceeded the upper calibration limit of the colorimetric tubes for the floor and tile cleaner. In repeated trials using higher capacity colorimetric tubes, ammonia volatilization from the floor and tile cleaner product led to airborne concentrations consistently exceeding 200 p.p.m. for 20–30 min after the spill, despite the bathroom window and door being opened after 15 min. Table 2 also illustrates much lower airborne ammonia levels after spilling about half the container (17 ounces) of the spray-on window cleaner. Ammonia levels measured at 2-ft height showed a consistent airborne concentration of 7–8 p.p.m. at between 4 and 10 min after the spill, while measurements at BZH (5-ft) were about half those observed at 2 ft during the same time period.

The ammonia concentrations above the spilled name brand spray-on product solution were lower than would be expected based on the volume spilled and the stated percent ammonia content (1–3% × 17 ounces) in comparison to the floor and tile cleaner (5% × 33 ounces). However, the measured product ammonia content was lower than that stated. For example, linear adjustment of the spray-on window cleaner data at BZH (e.g., 4 p.p.m. at 4–10 min) for the difference in measured percent ammonia (times 3/0.1%) and volume spilled (times 33.1 ounces/17.3 ounces) leads to an expected exposure concentration of about 230 p.p.m. above the spilled floor and tile cleaner. Instead, airborne ammonia concentrations under these conditions rose to >450 p.p.m. above the spilled floor and tile cleaner product.

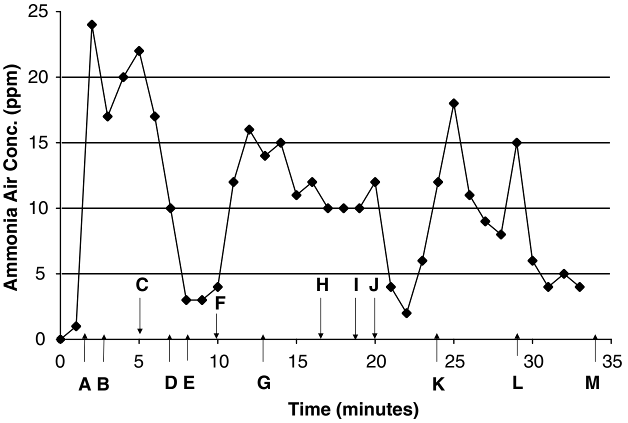

Figure 1. Airborne ammonia concentrations in three bathrooms during use of diluted floor and tile cleaner (0.1% ammonia), PAC-III Lapel Monitor. Letters denote the start time of the following events: (A) mixed 1 cup floor and tile cleaner with 2 gallons hot water in a bucket inside bathroom 1; (B) begin cleaning tile floor, vanity counter, sink, and small mirror of bathroom 1 with soaked sponge; (C) begin cleaning shower enclosure tile walls, floor and glass door; (D) end cleaning of bathroom 1 and transport equipment to bathroom 2; (E) set up equipment in bathroom 2; (F) begin cleaning tile floor in bathroom 2 with soaked sponge; (G) begin sponge cleaning of shower enclosure tile wall, floor and glass door, countertop, large vanity mirror, and tile surround and bathtub; (H) end cleaning bathroom 2 and transport equipment to bathroom 3; (I) set up equipment in bathroom 3; (J) begin cleaning tile floor in bathroom 3 with soaked sponge; (K) begin cleaning bathtub, surrounding tile and glass doors on tub enclosure; (L) begin cleaning vanity sink and small mirror; (M) end of cleaning in bathroom 3.

Exposures Assessed During Label-Directed Product Uses of Floor and Tile Cleaner

Standard Strength Cleaning Solution: 0.1% Ammonia The airborne ammonia sampling data for label-directed use of the floor and tile cleaner at standard cleaning strength (1 cup per 2 gallons) are summarized in Figure 1. The timing of specific activities and cleaning events in the three bathrooms are summarized in the footnote to Figure 1. Peak ammonia levels at BZH measured with the PAC III monitor (personal sample) occurred within 2–3 min after mixing a bucket full (2 gallons) of the floor and tile cleaner solution in the first and smallest bathroom (#1), whereas the other two larger bathrooms had peak levels occurring after about 5 min of cleaning activity using the same bucket of cleaner without further mixing events (Figure 1). Bathrooms 2 and 3 had peak exposures recorded during cleaning in the shower or tub enclosure, while bathroom 1 had peaks apparently associated with mixing the cleaner solution and after entry and cleaning in the shower enclosure. Peak exposure concentrations approached, but did not exceed the ACGIH 8-h TWA occupational exposure limit of 25 p.p.m., or the ACGIH and NIOSH-recommended short term exposure limit of 35 p.p.m., which is a more appropriate comparison point for these short-term (<10 min) peak exposure measurements.

Airborne ammonia levels based on area samples taken in the center of each bathroom at BZH (NIOSH 6015) are summarized in Table 3. The calculated TWA for these three area samples was 9.1 p.p.m. during cleaning activities, whereas the personal sample (also NIOSH 6015) collected during all the bathroom cleaning activities showed 10 p.p.m. Thus, there is good agreement between the area samples and personal sample ammonia levels determined using NIOSH Method 6015.

Table 3 also shows good agreement between the concurrent measurements utilizing NIOSH Method 6015 and the PAC III monitor, both of which were mounted to the collar/lapel of the person conducting the cleaning. The PAC III monitoring data (readings taken every 60 s) were averaged across the appropriate event-specific sampling periods to arrive at TWAs for comparison with the NIOSH Method 6015 data. Calculated values for the PAC III monitoring data show slightly higher average levels compared to the concurrent NIOSH Method 6015 results for the floor and tile cleaning activities (Table 3).

Double-Strength Cleaning Solution: 0.2% Ammonia Airborne ammonia profiles for bathroom tile cleaning in a

Table 3. Event-specific and time-weighted average ammonia air concentrations using two measurement methods.

Exposure event and sample type	Duration (min)	NIOSH method 6015 (p.p.m.)	PAC III monitor TWA (p.p.m.)
Bathroom 1 floor, tile and glass cleaning: area sample (NIOSH) and personal sample on lapel (PAC III)	7	9.4	11.9
Bathroom 2 floor, TILE and glass cleaning: area sample (NIOSH) and personal sample on lapel (PAC III)	9	13	12.1
Bathroom 3 floor, tile and glass cleaning: area sample (NIOSH) and personal sample on lapel (PAC III)	17	7	8.5
Calculated time-weighted average for all 3 bathrooms	33	9.1	10.2
Bathrooms 1, 2, and 3 floor, tile and glass cleaning: personal sample on lapel by NIOSH 6015 method		10	
Window cleaning: personal samples (NIOSH and PAC III Monitor)	15	0.65	1.1[a]

[a] Recorded values for the window cleaning activity were below the reliable detection limit of 3 p.p.m. for the PAC III monitor. The average of 15 measurements recorded every 60 s during window cleaning is reported.

separate home using double the standard strength cleaning solution are illustrated in Figure 2. Bathroom 4 and bathroom 5 were cleaned with the floor and tile cleaner solution at 0.2% ammonia content (1 cup per gallon). Both bathrooms had no active ventilation during the mixing and cleaning steps, although the entry doors remained open at all times. The cleaning steps included mopping the floor with a sponge-type mop and scrubbing spots on the floor with cleaner-soaked paper towels, but no cleaning was done of the vanity countertops or within the bathtub enclosure. Peak exposure during initial mopping reached about 90 p.p.m. in both bathrooms at 3–5 min after mixing the cleaner solution with continuous cleaning thereafter. Scrubbing with soaked paper towels on hands and knees did increase the measured ammonia exposure concentration as expected, but overall peak exposures seemed to correlate best with time since the cleaning began (and probably the total volume of ammonia cleaner spread over the surfaces cleaned). The average exposure concentration during cleaning was approximately 13–35 p.p.m. for the cleaning steps (time zero to end of cleaning) and 23 p.p.m. for the cleaning and ventilation steps (from time zero until the monitor returned to 0 p.p.m. after cleaning). Figure 2 also illustrates the rapid decline in airborne ammonia concentrations following the 0.2% cleaner usage, taking only 2–3 min to decline from 62 p.p.m.–11 p.p.m. in a bathroom with no forced ventilation other than opening the window (the entry door was open at all times).

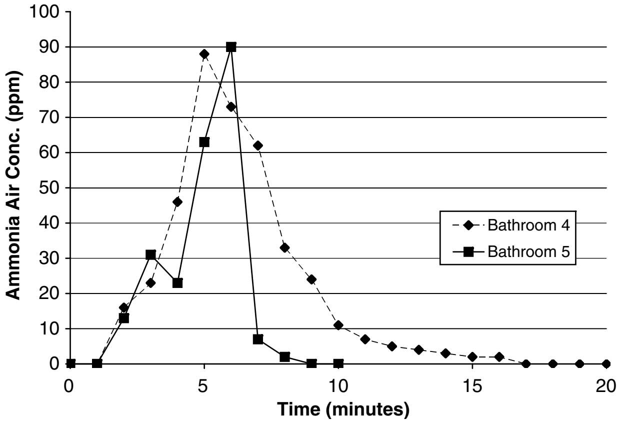

Figure 2. Airborne ammonia concentrations during bathroom tile cleaning with diluted floor and tile cleaner (0.2% ammonia), PAC-III Lapel Monitor. Relevant activities in bathroom 4: ($T = 1.5$) mixed 1 cup floor and tile cleaner with 1 gallon hot water in a bucket inside bathroom 4; ($T = 3$) soak sponge mop, wring lightly, and begin mopping the tile floor; ($T = 5$) scrub the tile floor with soaked paper towels while on hands and knees; ($T = 8.25$) end of cleaning, open window in bathroom to vent; and in bathroom 5: ($T = 1$) mixed 1 cup floor and tile cleaner with 1 gallon hot water in a bucket inside bathroom 5; ($T = 2$) scrub the tile floor with soaked paper towels while on hands and knees; ($T = 3$) soak sponge mop, wring lightly, and begin mopping the tile floor; ($T = 6$) end of cleaning in bathroom 5; ($T = 6.25$) remove monitor to outdoors to clear sensor.

Figure 3 presents the airborne ammonia profile for tile cleaning with the 0.2% ammonia solution in an open den area of the same home. A larger floor surface area, approximately 100 ft^2 of tile, was cleaned using both mopping while standing and scrubbing with soaked paper towels while on hands and knees. The peak ammonia level at 36 p.p.m. occurred within 2.5 min after mixing and then mopping the entire area once (at time = 2–4 min). Scrubbing the floor on hands and knees at time = 4–6 min did not lead to increasing exposure concentrations, again suggesting that total cleaner volume dispensed may be a better indicator of exposure potential than distance between the cleaning surface and one's breathing zone. The average exposure during cleaning (0–7 min) was about 16 p.p.m. and for cleaning and ventilation to nondetectable levels (0–17 min, inclusive) was approximately 11 p.p.m. In this scenario, a large sliding glass door was opened at time = 7 min (open area about 5 × 7 ft).

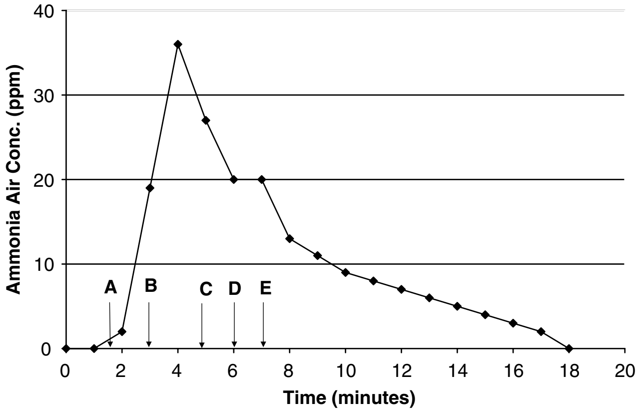

Figure 3. Airborne ammonia concentrations during den tile cleaning (100 ft^2) with diluted floor and tile cleaner (0.2% ammonia), PAC-III Lapel Monitor. Letters denote the start time of the following events: (a) mixed 1 cup of floor and tile cleaner with 1 gallon hot water in a bucket in den area; (b) soak sponge mop, wring lightly, and begin mopping tile floor; (c) scrub the tile floor with soaked paper towels while on hands and knees; (d) end of cleaning in den area, bucket and soaked towels were left in the cleaned area; (e) opened sliding glass door to vent, but monitor remained in cleaned area at BZH.

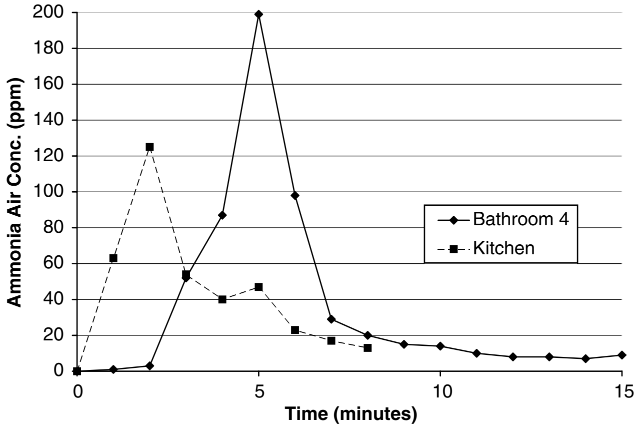

Figure 4. Airborne ammonia concentrations during bathroom countertop cleaning with concentrated floor and tile cleaner (3% ammonia), PAC-III Lapel Monitor. Relevant activities in bathroom 4: ($T = 2$) pour four tablespoons of floor and tile cleaner on countertop and spread with dry paper towels; ($T = 4$) end of cleaning in bathroom but remained in front of vanity and placed the used paper towels in an open-top bathroom garbage can; ($T = 5.5$) opened window in bathroom; ($T = 13.5$) monitor placed outdoors to clear sensor; and in the kitchen: ($T = 0.25$) poured 4 tablespoons of undiluted floor and tile cleaner on countertop and spread with dry paper towels; ($T = 2.25$) completed wiping, placed the used paper towels in kitchen garbage can inside a cabinet under the kitchen sink; ($T = 3.5$) continued standing in front of cleaned countertop; and ($T = 4.5$) monitor placed outside to clear the sensor.

The ammonia vapors dissipated more slowly compared to the bathrooms (Figure 2) where the floor surface cleaned (and cleaner volumes dispersed) were much lower. There was no forced ventilation in the den area other than opening the sliding glass door.

Full Strength Concentrate Cleaner Usage: 3% Ammonia

Figure 4 presents the airborne ammonia profile for use of a small volume (4 tablespoons) of the full strength floor and tile cleaner to clean the countertops in bathroom 4. The peak ammonia level at 200 p.p.m. occurred within 3 min after pouring 4 tablespoons of the concentrate onto a 12 ft^2 countertop and immediately spreading it with dry paper towels. The peak ammonia levels in the bathroom space declined rapidly after the bathroom window was opened at time = 5.5 min. The average exposure during cleaning steps (about 0–4 min) was about 63 p.p.m. and for the entire period monitored (0–16 min) was about 33 p.p.m.

Figure 4 also presents a countertop cleaning scenario with 4 tablespoons of the concentrate used on the 21 ft^2 kitchen countertop. The countertop area and the room volume were much larger for the kitchen compared to bathroom 4, and the kitchen was open to the den area. The peak ammonia concentration of 125 p.p.m. occurred within 2 min after pouring the concentrate onto the countertop and immediately spreading it to sanitize the surfaces. The average exposure concentration was about 56 p.p.m. during the cleaning steps (0–4 min).

Two additional studies were attempted to examine ammonia exposure concentrations for cleaning with 4 tablespoons of the 3% solution on soaked paper towels inside the tub enclosures of bathrooms 4 and 5 with the enclosure door left open. In each case, the PAC-III monitor detected rapidly rising concentrations (increasing by 50–80 p.p.m. per minute) that exceeded 200 p.p.m. within 2.5 min after the tile cleaning inside the tub enclosure began (data not shown). In both trials, irritation of eyes and nasal passages was intolerable to the cleaner once ammonia concentrations approached 200 p.p.m. and hence the full concentration *versus* time profiles were not obtained.

Exposures During Label-Directed Use of the Name Brand Glass Cleaner Product

Airborne ammonia concentrations measured during the window cleaning activity using the spray-on glass cleaner were considerably lower than those for use of the floor and tile cleaner at comparable ammonia strength (0.1%. solution). The volume of cleaner used in this cleaning scenario was approximately 0.3 ml per square foot of glass cleaned. The PAC III monitoring data varied between 0 and 2 p.p.m. during window cleaning activity, but these recorded levels are below the instrument manufacturer's reliable detection limit of 3 p.p.m. (data not shown). Table 3 shows that the personal sample analyzed according to NIOSH Method 6015 showed an exposure concentration of 0.65 p.p.m. for the window cleaning activity. The concurrent data from the PAC III monitor averaged 1.1 p.p.m., which despite detection limit issues tends to reinforce the relatively low exposure levels associated with a typical use of this window cleaner product. Similar use of the store brand glass cleaner (0.05%) led to low airborne ammonia exposures as well (0–2 p.p.m. using the PAC-III lapel monitor, data not shown). The floor and tile cleaner product used at 0.1% strength led to about 14-fold higher TWA exposures than for use of the name brand window cleaner at similar ammonia strength (NIOSH Method 6015 results, Table 3), This differential must be due in large part to the much smaller volume of solution dispensed with the window cleaner pump sprayer.

Discussion

This study provides information on the pattern and magnitude of airborne ammonia concentrations from limited spill scenarios and for selected label-directed household cleaning uses of two common types of ammonia-containing products in various indoor settings. No similar cleaning exposure studies or data sets were identified in our searches of the published literature to date. Our data indicate distinct differences in exposure potential between two spray-on window cleaner products at ready-to-use concentrations and a household floor and tile cleaner product with label-recommended uses for full strength and various diluted cleaning solutions.

A recent study by Webb et al. (2002) reported on ammonia concentrations in a room-size study chamber (1720 ft^3) in which they assessed nicotine desorption from furniture and wall surfaces exposed to environmental tobacco smoke when a bucket of household ammonia cleaner (2 cups in 1 gallon of hot water) was placed inside. The dissolved ammonia concentration was not reported, but would correspond to about 0.4% if their household cleaner had 3% ammonia like the product we studied. They reported a peak concentration of 30 p.p.m. airborne ammonia at 2 h after placing the bucket inside the room. This was a vapor equilibrium study, not a cleaning study. Although the experimental conditions are quite different from the current study, their peak ammonia level of 30 p.p.m. may be compared with our peak of 36 p.p.m. for the den tile floor cleaning scenario with a 0.2% ammonia solution.

The current study findings indicate that the potential for excessive consumer exposures to airborne ammonia is much greater for the household floor and tile cleaner product during accidental spills or in expected uses involving poorly ventilated spaces or use of stronger cleaning solutions than the standard dilution (0.1%) directed on the product label. In contrast, the window cleaner product did not demonstrate potential for excessive airborne ammonia exposures in the simulated accidental spill or expected use scenarios. While the room size and air exchange rate were very different for the expected use scenarios between the two products, the spill study data clearly show a far greater exposure potential with the floor and tile cleaner product.

There are several uncertainties and caveats that should be noted with respect to these data. First, we did not attempt to fully characterize the indoor environment conditions and other cleaner volume parameters that might be useful to accurately model indoor ammonia concentrations. We did not assess mass balance, airflow characteristics or humidity, and did not attempt to measure the volume of cleaner used in most of the cleaning scenarios presented. However, we believe that the cleaning scenarios in the current study are representative of common household usages. Thus, the application of these data to other situations should consider the limitations of this study. Second, we discovered that the ammonia content information listed on a container or on the MSDS may not be accurate, and may only indicate an upper bound content. Products like the window cleaners tested here are only required to list ammonia content on the product MSDS if it exceeds 1% (wt/vol). Plus, the MSDS does not have to list the precise formula or content of ammonia; rather, it must list a not-to-exceed level or range if the final formulated product could contain $>1\%$ ammonia. Third, we encountered problems with determining the product ammonia content when utilizing a second USEPA-certified laboratory that was not certified for consumer product and pharmaceutical analyses (Good Manufacturing Practices Certification). Results obtained using the Total Kjeldahl Nitrogen method in the second laboratory were similar for the concentrate floor and tile cleaner (31,000 mg/l). However, the ready-to-use glass cleaners were reported to contain 2–4-fold higher concentrations than expected based on the other laboratory, and there were analytical problems encountered in digesting the diluted samples. Thus, we relied solely on the other laboratory's results (Table 1) that had good quality control information.

Review of Dose–Response considerations

Owing to the natural presence of ammonia in sewage, fertilizers, animal excreta, and other processes there is a constant background exposure to airborne ammonia in the ambient air. Several researchers have examined background air concentrations not influenced by local sources and determined that low part per billion (p.p.b.) ammonia levels, for example, 0.1–5 p.p.b., are common in both urban and rural areas throughout the world (Georgii and Gravenhorst, 1977; Farmer and Dawson, 1982; Harward et al., 1982; Tanner, 1982; Crutzen, 1983; Dawson and Farmer, 1984; Kelly et al., 1984; Russell et al., 1988; Fangmeier et al., 1994; Aneja et al., 1998). Similar levels have been reported for airborne ammonia concentrations over the world's oceans (Georgii and Gravenhorst, 1977).

Controlled ammonia exposure studies have shown sensory irritation in unadapted individuals exposed at 20–30 p.p.m. for 10–15 min (Vigliani and Zurlo, 1956; MacEwen et al., 1970; Industrial Bio-Test Laboratories, 1973; Verberk, 1977; Sekizawa and Tsubone, 1994); however, tolerance is commonly observed with repeated exposures (Verberk, 1977; Sekizawa and Tsubone, 1994). Other acute exposure studies in humans further demonstrate moderate to severe respiratory and ocular irritation from airborne ammonia exposures at or above 50 p.p.m. Silverman et al. (1949) exposed volunteers to 500 p.p.m. ammonia for 1.5 h and observed lacrimation, nasal, and throat irritation, and increased minute volume and respiratory rate. Industrial Bio-Test (1973) reported on volunteers exposed to ammonia vapors for 5 min and observed nasal and throat irritation at 72 p.p.m., but not at 50 p.p.m. Cole et al. (1977) exposed male volunteers to ammonia vapors for 8–11 min while exercising and observed decreased minute volume and increased tidal volume at 150–331 p.p.m., but not at 100 p.p.m. Verberk (1977) exposed volunteers to 50 p.p.m. ammonia vapors for 1.5 h and observed nose and throat irritation, urge to cough, and eye irritation.

Longer-term studies reveal a pattern of tolerance to irritation symptoms and no demonstrated pulmonary function deficits for ammonia exposures below 25 p.p.m. Ferguson et al. (1977) reported a study of intermediate exposure duration for volunteers exposed at 50 or 100 p.p.m. ammonia for six weeks (6 h per day, 5 days per week) and reported transient eye, nose, and throat irritation at 100 p.p.m. but not at 25 or 50 p.p.m.; these exposures were not associated with any clinical changes in lung function tests, physical examination findings, or performance of normal job duties. Holness et al. (1989) reported that chronic occupational exposure to average levels of 12.5 p.p.m. ammonia in a group of soda ash factory workers did not cause clinical changes in pulmonary function tests or odor sensitivity. Ballal et al. (1998) reported a cross-sectional study of asthma and respiratory complaints among male workers at two fertilizer factories. They reported that workers exposed to ammonia levels generally above 25 p.p.m. had significantly higher risks of respiratory symptoms and asthma, particularly for those in Factory 1 where airborne ammonia levels ranged from about 3 to 184 p.p.m. Workers in Factory 2 where ammonia exposure levels were always below 25 p.p.m. (range 0.03–10 p.p.m.) reportedly did not have significantly elevated risks for respiratory symptoms or asthma.

ATSDR (2002) developed a minimal risk level (MRL) for acute inhalation exposure at 1.7 p.p.m. based on the Verberk (1977) study showing mild irritation in humans at 50 p.p.m. × 2 h, and a chronic inhalation MRL at 0.3 p.p.m., based on the soda ash worker study by Holness et al. (1989) showing no respiratory effects after chronic occupational exposures (average 14 years employment) averaging 12.5 p.p.m. The US Environmental Protection Agency (USEPA; IRIS, 2003) derived a similar chronic standard for ammonia inhalation called the reference concentration (RfC) at 0.1 mg/m^3, equivalent to about 0.14 p.p.m. Both the MRL and RfC values are developed to apply to assumed continuous exposures to the general population, and incorporate various modifying factors and uncertainty factors to account for potentially sensitive individuals. However, these concentrations are well below those that have been demonstrated to have adverse health effects in humans.

Recommended workplace exposure limits are based on assumed exposure to healthy workers for 8–10 h per day, and hence are less conservative than the general population safe exposure estimates (MRL and RfC). Although the OSHA permissible exposure limit (PEL) remains at 50 p.p.m. as an 8-h TWA, the NIOSH recommended exposure limit and the ACGIH (2001) threshold limit value are set at 25 p.p.m. as an 8-h TWA. The short-term exposure limit (15-min TWA) recommended by NIOSH and ACGIH is 35 p.p.m. ammonia.

Product-Specific Hazard Assessment

As illustrated in the spill exposure study, a bathroom spill of about 33 oz of 3% ammonia may produce inhalation exposures as high as 550 p.p.m. airborne ammonia, even with window ventilation and the bathroom door open. These exposures far exceed the current occupational and environmental safety limits for acute inhalation exposure including the ACGIH and NIOSH short-term exposure limit of 35 p.p.m. (15-min average), the ATSDR minimal risk level for acute exposures (1.7 p.p.m.), and the two most restrictive AIHA emergency response planning guidelines (ERPG-1 = 25 p.p.m. and ERPG-2 = 200 p.p.m.). Airborne ammonia levels after such a spill exceeded 200 p.p.m. for at least 15–25 min after the spill within a bathtub/shower enclosure. Extended exposures at concentrations above 300 p.p.m. could cause significant respiratory tract and ocular irritation in normal adults or children, but may pose more severe risks to persons with asthma or certain other pulmonary diseases. However, these exposures involving spills and usage of 3% ammonia in household settings generally dissipate quickly enough to avoid clinically important corrosive damage to the lungs as is observed with exposures >5000 p.p.m. even for a matter of minutes. Overall, the warning properties of ammonia should be sufficient to induce avoidance actions in most situations, unless egress was impeded following a spill.

In contrast, the spill exposure study for the spray-on window cleaner product showed peak exposures at BZH that were below 5 p.p.m. This occurred despite the finding that the high pH (10.9) of glass cleaner solutions indicates the vast majority of dissolved ammonia was in the form of volatile NH_3 gas, not ammonium ion. In the product spill scenario, it seems unlikely that the spray-on window cleaner would lead to hazardous airborne ammonia levels. The airborne ammonia exposures during the window cleaner spill were lower than expected; we did not specifically investigate this issue, but speculate that other surfactants or solvents (ethylene glycol *n*-hexyl ether, and isopropanol) added to the window cleaner may impede ammonia vapor release from the aqueous solution. Moreover, normal use of this ready-to-use aerosol pump product would not require removal of the cap/pump mechanism except perhaps for refilling.

The label-directed uses of the floor and tile cleaner product led to short-term exposures that for the standard cleaning solution strength (1 cup per 2 gallons or about 0.1%) averaged around 10 p.p.m. airborne ammonia and showed peak values between 16 and 24 p.p.m. These peak exposure levels approach but do not exceed the ACGIH/NIOSH short-term exposure limit of 35 p.p.m., and the average exposure level in ventilated bathrooms was less than half of the NIOSH and ACGIH occupational exposure limit recommendation of 25 p.p.m. as an 8-h TWA. However, subsequent studies using the 0.2% ammonia solution led to peak exposures of around 90 p.p.m. in two small, unventilated bathrooms and 36 p.p.m. in a more open den area while mopping and scrubbing tile floors. These product usage conditions can readily lead to peak and average exposures to consumers at or above the recommended occupational short-term exposure limits, but dissipate relatively quickly over the following 10–15 min without forced ventilation. Also, as noted above, individuals with potentially greater sensitivity to respiratory effects from irritant exposures, for example, asthmatics, may still experience acute respiratory problems even under these peak exposure concentrations (e.g., 36–90 p.p.m.).

We also examined exposures for use of the concentrate (undiluted) floor and tile cleaner for sanitizing countertops or the tile inside tub enclosures. Use of just a few tablespoons of the undiluted cleaner on countertops in an open kitchen area or in a small bathroom led to peak ammonia concentrations between 100 and 200 p.p.m. within 1–2 min after dispensing the product. Again, the airborne ammonia levels dissipated within a few minutes, except in more contained spaces like a bathtub enclosure. Thus, using the concentrate (3% solution) in large volumes and/or in contained spaces can lead to exposures exceeding the ERPG-2 guideline of 200 p.p.m.

The label-directed use of the spray-on window cleaner product led to much lower short-term ammonia exposures (about 0.7 p.p.m.) compared to the floor and tile cleaner at 0.1% (average 10 p.p.m.) and 0.2% solutions (average about 11–30 p.p.m.). The intentional generation of coarse spray aerosols by the mechanical pump dispenser did not lead to substantial exposures (<2 p.p.m.). Indeed, the pump mechanism appears to simultaneously limit the total volume of cleaner (including ammonia) dispensed, and prevent appreciable vaporization losses of ammonia remaining in the bottle of cleaning solution. Accordingly, there appears to be no substantial inhalation hazard associated with normal cleaning uses of the ammonia-containing spray-on window cleaner product.

Our data on exposure and hazard potential for the products under study correlate with the medical consequences of domestic users reported in a recent compilation of data from US poison control centers (Watson et al., 2003). In 2002, there were 2418 reported exposures to household ammonia cleaners (e.g., floor and tile cleaners) with 437 (18.1%) resulting in treatment at a health care facility and 163 of those (163/437 or 37.3%) with moderate to major outcomes. For household glass cleaners with ammonia, 1564 exposures were reported with 127 (8.1%) treated in health care facilities and only 20 (15.7%) with moderate outcomes. No deaths were reported from either type of household ammonia exposure, but children under age 6 years comprised 78% of reported exposures involving glass cleaner and only 40% of exposures involving ammonia cleaners. These statistics do not distinguish inhalation exposures from ingestion exposures that are particularly common in young children. Inhalation exposures from all fumes, gases, or vapors comprised about 3.5% of all poison control center calls in 2002, but those attributable to ammonia were not delineated. Nazaroff and Weschler (2004) note that many poisoning incidents may involve reaction products of improperly combining household cleaners, as in chloramine gas generation from combining household ammonia and bleach. They also reported that at least 26 case reports implicate cleaning or cleaning products as the cause of respiratory impairment, although only one of the cited reports involved ammonia vapors as the suspect toxic agent.

Most consumers would be expected to take protective actions to avoid ammonia exposures when atmospheric levels produce sensory irritation, for example, at exposure concentrations above 25–50 p.p.m. Significant respiratory irritation from spills or usage of the household ammonia cleaner studied here can be avoided by assuring that adequate ventilation is used and/or that persons are evacuated from the impacted area until the emission source has been largely exhausted. Persons with pre-existing respiratory conditions such as asthma or other obstructive lung diseases are generally considered to be at increased risk of adverse health consequences from exposure to atmospheric irritants like ammonia. The short-term exposure limits for workplace ammonia exposures (35 p.p.m.) may not be sufficiently low to protect these individuals from experiencing respiratory effects during spillage and certain uses of concentrated household ammonia products like the floor and tile cleaner examined in the current study.

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