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ABSTRACT

Nicotine is a major constituent of environmental tobacco smoke. Sorptive interactions of nicotine with indoor surfaces can substantially alter indoor concentrations. The phenomenon is poorly understood, including whether sorption is fully reversible or partially irreversible. We hypothesize that acid-base chemistry on indoor surfaces might contribute to the apparent irreversibility of nicotine sorption under some circumstances. Specifically, we suggest that nicotine may become protonated on surfaces, markedly reducing its vapor pressure. If so, subsequent exposure of the surface to gaseous ammonia, a common base, could raise the surface pH, causing deprotonation and desorption of nicotine from surfaces. A series of experiments was conducted to explore the effect of ammonia on nicotine sorption to and reemission from surfaces. Our results indicate that, under some conditions, exposure to gaseous ammonia can substantially increase the rate of desorption of previously sorbed nicotine from common indoor surface materials.

KEY WORDS

Pollutant sorption and desorption, Indoor air chemistry, Environmental tobacco smoke, Laboratory and field experiments, VOCs and SVOCs

INTRODUCTION

Nicotine is a major organic constituent of environmental tobacco smoke (ETS). Typical time-averaged concentrations of nicotine in homes with smokers are $\sim 2\text{-}4 \mu\text{g}/\text{m}^3$ (Coultas et al., 1990; Leaderer and Hammond, 1991). Nicotine is also a strongly sorbing compound. Experiments have shown that sorption onto indoor surfaces significantly reduces concentrations that result from recent emissions (Singer et al., 2002). Gradual reemission of sorbed nicotine could increase exposures during periods without smoking.

Recent studies of nicotine interactions with surface materials have explored the sorption process (Piade et al., 1999; Van Loy et al., 2001); however, it is unclear from the existing evidence whether uptake is fully reversible or partially irreversible. For assessing exposure to nicotine, and for using it as a tracer of exposure to environmental tobacco smoke, the implications of partially irreversible versus fully reversible sorption are large.

Nicotine is a diprotic base that is emitted in the particle phase of sidestream smoke, but quickly partitions to the gas-phase in environmental tobacco smoke (Neurath et al., 1991). Pankow et al. (1997) explored the significance of acid-base chemistry on the partitioning of nicotine between the gas and particle phases in mainstream cigarette smoke. They suggested that ammonia plays a key role in influencing nicotine phase partitioning. Nicotine, which initially is bound to the particle phase in a lower volatility, monoprotonated form is thought to lose the proton as pH rises due to the effect of ammonia. The higher volatility, nonprotonated nicotine then partitions more readily to the gas phase.

This line of reasoning led us to consider whether a similar process might explain the process by which nicotine associated with environmental tobacco smoke sorbs to indoor surfaces. We hypothesize that nonprotonated nicotine may sorb to surfaces when ETS concentrations are high and then become protonated in an acid-base surface reaction. The less volatile form bound to the surface would appear to be irreversibly sorbed; however, the process may be reversed by reactions with ammonia (or other bases) that increase surface pH. Nonprotonated nicotine could then desorb more readily from the surface and re-enter the gas-phase.

Ammonia is the most common basic gas in the atmosphere, and major indoor sources include human activities, household cleaners, and litter boxes. Indoor concentrations in homes are typically in the ppb range but can reach tens of ppm during the use of ammonia-based cleaners (Atkins and Lee, 1993).

This paper presents our initial investigation into the effect of ammonia on sorptive interactions between nicotine and indoor surfaces.

EXPERIMENTAL METHODS

Two sets of experiments were conducted in a small glass chamber with a volume of 60 L and a surface area of approximately 1 m². In the first experiment, all of the surfaces were lined with a layer of gypsum wallboard that had been coated with low-VOC latex paint. In the second experiment, the wallboard was removed and all surfaces of the chamber were lined with nylon carpet (without any cushion).

Chamber air temperature was controlled between 20-24 °C and relative humidity was in the range of 35-55% during all experiments. Clean dry air was supplied to the chamber from a gas cylinder, and the flow was split such that part of the flow passed through a humidifier to obtain the desired range of relative humidity. The air exchange rate was approximately 0.5 h⁻¹ during all experiments.

After pre-conditioning the chamber with clean air and measuring background concentrations, nicotine was introduced using a diffusion tube held at a constant temperature of 30 °C. The diffusion rate was approximately 50 ng/min in a 50 ml/min flow of nitrogen. Nicotine was supplied until concentrations inside the chamber stabilized, indicating that a dynamic equilibrium between sorption and desorption had been reached. The nicotine source was removed, and nicotine concentrations were monitored until they stabilized again. Ammonia was then introduced into the chamber using a permeation tube held at a constant temperature of 30 °C. The supply rate was approximately 2500 ng/min in a 100 ml/min flow of nitrogen. Both the wallboard and carpet experiments were conducted in this manner except that in the carpet experiment the nicotine source was not removed before introducing ammonia.

During the experiments, nicotine and ammonia samples were collected on sorbent tubes inserted through ports in the chamber wall. Air was sampled at a rate of 100 ml/min using pumps and mass-flow controllers located outside of the chamber. Nicotine samples were collected on Tenax sorbent tubes that were thermally desorbed and analyzed by GC/MS. Ammonia samples were collected on sulfuric-acid-treated, silica gel samplers that were extracted and subsequently analyzed using an ammonia-sensing electrode. When duplicate samples were obtained, the results were averaged to calculate concentrations.

A set of three additional experiments was conducted in a room-size chamber furnished with various residential materials. The chamber had a volume of 49.5 m³, floor dimensions of 4.61

m by 4.42 m, and a height of 2.43 m. During the first two experiments, the chamber was fully furnished (FF). The ceiling and walls were lined with 64.2 m² of gypsum wallboard finished with low-VOC latex paint, and the floor was lined with 20.4 m² of residential nylon carpet. The furnishings had a total surface area of approximately 43.2 m² and included draperies, wood and wood-laminate pieces, and upholstered chairs. During the third experiment, all furnishings were removed leaving only the wallboard and carpet (WBC).

Prior to the experiments reported here, the room-sized chamber had been exposed to ETS. The surfaces were thereby preconditioned with approximately 3200 mg of nicotine sorbed to all surfaces. Background samples of nicotine and ammonia were collected before beginning each set of experiments. All samples were collected and analyzed in the manner described earlier. Chamber air temperature and relative humidity were not controlled and were in the range of 20-24 °C and 33-56%, respectively, during experiments. Clean air was supplied to the chamber by drawing outside air through activated carbon, and the ventilation rate was held constant at 0.3 h⁻¹. Four small fans were present in the chamber to mix the air.

After measuring background concentrations of nicotine, ammonia was introduced into the chamber by diluting 0.24 L (2 cups) of a household ammonia cleaning solution in 3.8 L (1 gal.) of hot water. The bucket containing the mixture was placed in the center of the chamber, and nicotine and ammonia samples were collected for the following three days. At the end of the third day, the bucket was removed and the chamber was flushed with clean air for four days or more before beginning the next set of experiments.

RESULTS AND DISCUSSION

Results from experiments conducted in the small chamber are presented in Figures 1 and 2.

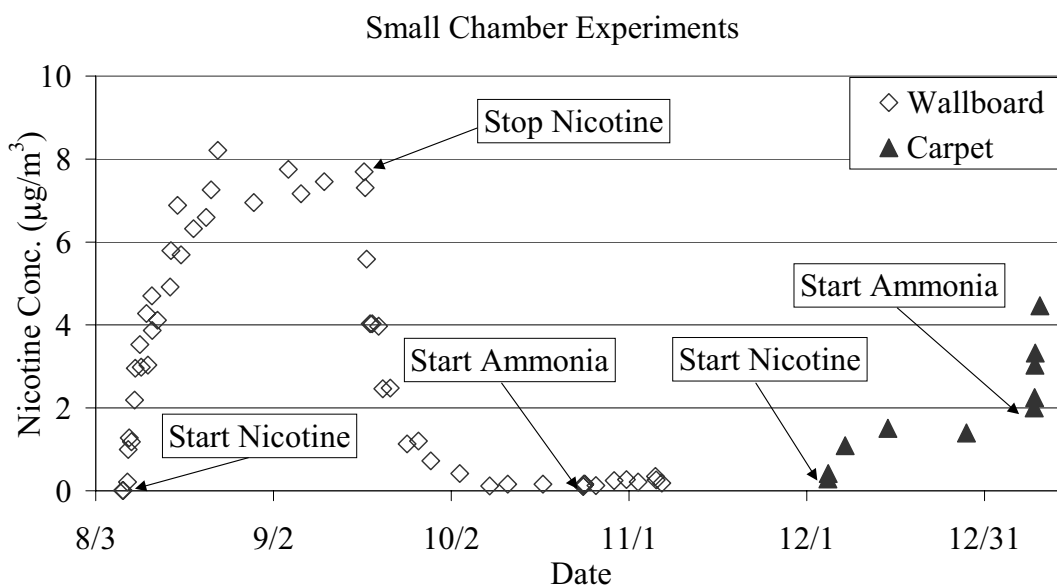


Figure 1. Nicotine concentrations in small chamber during wallboard and carpet experiments

In the first experiment, the chamber was lined with painted gypsum wallboard and the nicotine concentrations stabilized at ~ 8 µg/m³ six weeks after first introducing the nicotine into the chamber. During this time, the nicotine was sorbing to the wallboard surfaces thereby reducing the observed airborne concentrations from ~ 100 µg/m³ that would be expected if sorption were not occurring. After six weeks, the nicotine source was removed and

concentrations inside the chamber declined to $\sim 0.1 \mu\text{g}/\text{m}^3$ over the course of another four weeks. Ammonia was then introduced to the chamber. In this case, there was no noticeable increase in nicotine concentrations. Ammonia concentrations remained below 1.5 ppm, indicating a net loss to surfaces, since the level in supply air was ~ 7 ppm. This result suggests that the wallboard material provided a sink for both the nicotine and ammonia and that in this case nicotine desorption was unaffected by acid-base chemistry.

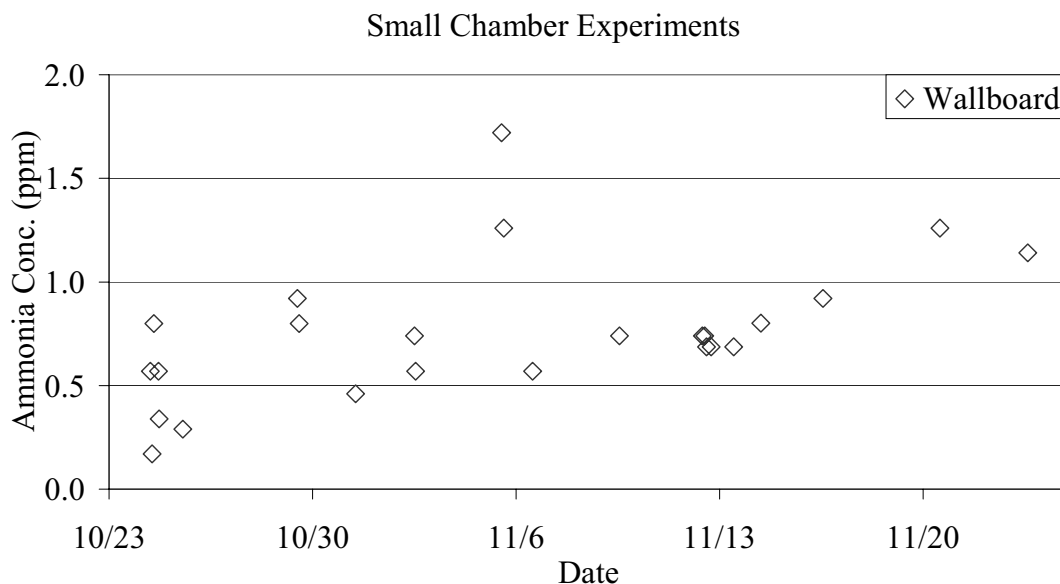


Figure 2. Ammonia concentrations in small chamber during wallboard experiment

In the second experiment, the chamber was lined with nylon carpet. Once again, sorption of nicotine to the surface material reduced airborne concentrations from the expected value of $100 \mu\text{g}/\text{m}^3$ without sorption to $\sim 2 \mu\text{g}/\text{m}^3$, even after four weeks. This time the nicotine source was not removed before the ammonia was introduced into the chamber. Within 24 hours of introducing the ammonia, the nicotine concentrations in the chamber increased to $4.5 \mu\text{g}/\text{m}^3$. This result indicates that acid-base chemistry did affect the partitioning of nicotine between the sorbed phase on the carpet and the gas phase.

Results from experiments conducted in the large chamber are presented in Figures 3 and 4. In the first set of experiments, the chamber walls and ceiling were lined with painted gypsum wallboard, the floor was lined with nylon carpet, and the room was fully furnished (FF) as described previously. Background samples were collected before introducing ammonia into the chamber, and in all cases nicotine concentrations were $\sim 1 \mu\text{g}/\text{m}^3$ and ammonia concentrations were less than 1 ppm. In both fully furnished experiments, the ammonia concentrations peaked at ~ 11 ppm, 60-90 minutes after introducing the ammonia solution into the chamber. In the first furnished experiment, nicotine concentrations peaked at $45 \mu\text{g}/\text{m}^3$, while in the second experiment nicotine levels rose to $14 \mu\text{g}/\text{m}^3$ inside the chamber. The lower nicotine concentrations measured in the repeat experiment might be explained by considering that only a small fraction of the total adsorbed nicotine may have been available at the surface to be liberated by acid-base interactions. Much of this available nicotine might have been re-emitted during the first experiment resulting in lower peak concentrations during the second trial.

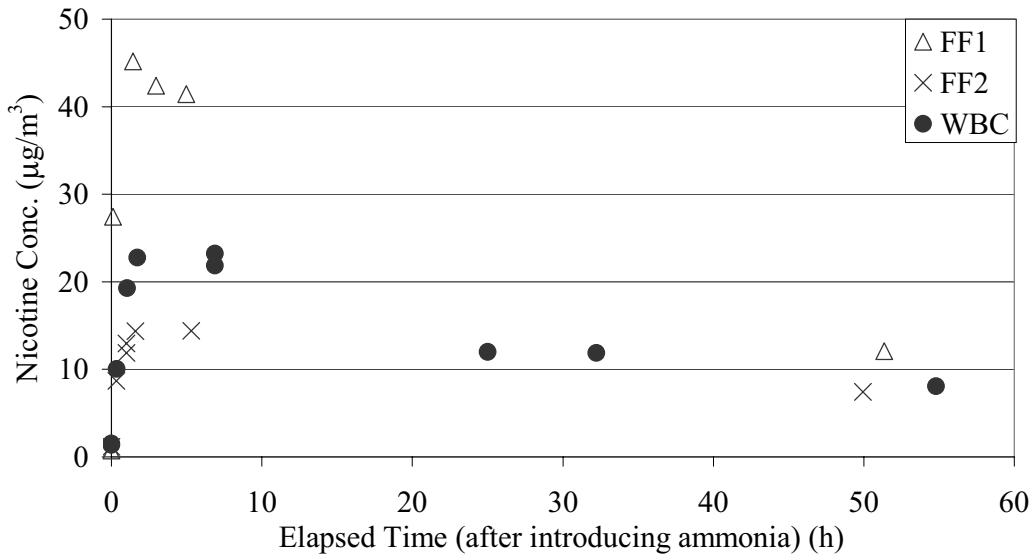


Figure 3. Nicotine concentrations in large chamber

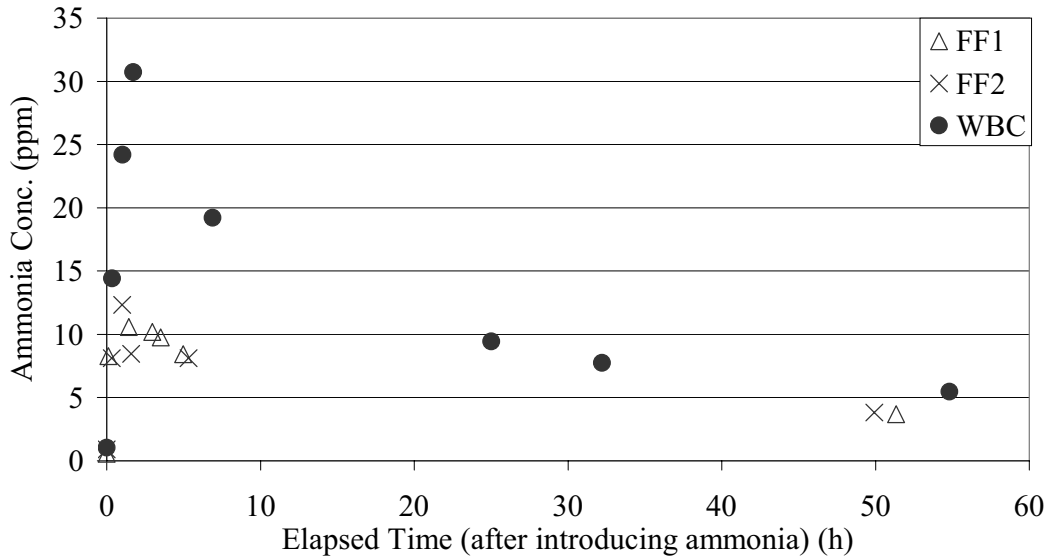


Figure 4. Ammonia concentrations in large chamber

In the final experiment, all of the furnishings were removed from the large chamber leaving only the wallboard and carpet (WBC). During this experiment, the ammonia concentrations peaked at 30 ppm approximately two hours after introducing the ammonia solution into the chamber. This peak concentration is three times higher than the peak observed in the previous two experiments. A possible explanation for this increase is that during the fully furnished experiments a large fraction of the ammonia was sorbing to the furniture, resulting in reduced airborne ammonia concentrations. The nicotine concentrations during the third experiment peaked at 23 µg/m³, which is between the peak values for the first two rounds. This may be because elevated ammonia levels in the chamber resulted in an increased nicotine reemission rate from what might otherwise have been observed at lower ammonia concentrations.

CONCLUSION

These experiments have demonstrated that acid-base chemistry on surfaces can play a potentially significant role in altering indoor concentrations of certain pollutants. To better

characterize such processes, it is important to consider the physical properties of the surface materials as well as the chemical properties of the pollutants of interest. The results of these specific experiments have shown that nicotine sorbs strongly to both wallboard and carpet. Increased reemission due to interactions with gaseous ammonia appears to be significant for carpet but not for wallboard. Common furnishings appear to provide additional sites for reversible nicotine sorption that is subject to gaseous ammonia effects. These experiments provide a basis for further study that could examine the effects of different chemicals, surface materials, relative humidity, and pH. Improving our understanding of the role of acid-base surface chemistry could aid in the development of more accurate sorption models as well as help determine how interactions of this nature may influence indoor air quality.

ACKNOWLEDGEMENTS

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REFERENCES

- Atkins DHF, and Lee DS. 1993. Indoor concentrations of ammonia and the potential contribution of humans to atmospheric budgets. *Atmospheric Environment*. Vol. 27A (1), pp 1-7.
- Coultas DB, Samet JM, McCarthy JF, *et al.* 1990. Variability of measures of exposure to environmental tobacco smoke in the home. *American Review of Respiratory Disease*. Vol. 142 (9), pp 602-606.
- Leaderer BP, and Hammond SK. 1991. Evaluation of vapor-phase nicotine and respirable suspended particle mass as markers for environmental tobacco smoke. *Environmental Science & Technology*. Vol. 25 (4), pp 770-777.
- Neurath GB, Petersen S, Dunger M, *et al.* 1991. Gas-particle phase distributions and decay rates of constituents in ageing environmental tobacco smoke. *Environmental Technology*. Vol. 12, pp 581-590.
- Pankow JF, Mader BT, Isabelle LM, *et al.* 1997. Conversion of nicotine in tobacco smoke to its volatile and available free-base form through the action of gaseous ammonia. *Environmental Science & Technology*. Vol. 31 (8), pp 2428-2433.
- Piade JJ, D'Andres S, and Sanders EB. 1999. Sorption phenomena of nicotine and ethenylpyridine vapors on different materials in a test chamber. *Environmental Science & Technology*. Vol. 33 (12), pp 2046-2052.
- Singer BC, Hodgson AT, Nazaroff WW, *et al.* 2002. Vapor-phase organics in environmental tobacco smoke: 1. Effects of smoking rate, ventilation, and furnishing level on apparent emission factors. *Environmental Science & Technology*. in press.
- Van Loy MD, Riley WJ, Daisey JM, *et al.* 2001. Dynamic behavior of semivolatile organic compounds in indoor air. 2. Nicotine and phenanthrene with carpet and wallboard. *Environmental Science & Technology*. Vol. 35 (3), pp 560-567.