

The influence of ammonia and carbon dioxide on the sorption of a basic organic pollutant to a mineral surface

Abstract Indoor surfaces have a sorptive capacity for organic pollutants which may be significantly influenced by other gases and the pH of the surface. In this research, we examine the influence of a common indoor gaseous acid, CO₂, and base, NH₃, on the adsorption of a volatile organic base, trimethylamine (TMA), to a mineral surface, zirconium silicate beads. Varying ammonia and CO₂ within concentration ranges of indoor relevance substantially influences the sorptive capacity of this mineral surface. Increasing the CO₂ mixing ratio to 1000 p.p.m. enhances surface capacity of TMA by 40–50%; increasing the NH₃ mixing ratio to 10 p.p.m. decreases the TMA surface capacity by ~5–80% depending on relative humidity. The phenomena of dissolution of TMA into bulk surface water and acid-base chemistry in the surface water do not adequately describe equilibrium adsorption on this surface. Instead, adsorption to the dry solid or to adsorbed water layers appears to dominate. Reduction in the equilibrium partition coefficient, k_e , in the presence of NH₃ is due to a competition between TMA and ammonia molecules for adsorption sites. Site competition appears to follow the Langmuir competitive model and most k_e values range from 0.003–0.045 m.

**M. Ongwandee, S. S. Bettinger,
G. C. Morrison**

University of Missouri-Rolla, Rolla, MO, USA

Key words: Adsorption; Absorption; Surface chemistry; Acidity; Amine; Surface characterization.

Glenn C. Morrison
University of Missouri-Rolla
221 Butler-Carlton Hall
Rolla, MO 65409
USA
Tel.: (573) 341 7192
Fax: (573) 341 4729
e-mail: gcm@umr.edu

Received for review 5 January 2005. Accepted for publication 20 May 2005.

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Practical Implications

Sorptive interactions with indoor surfaces strongly influence indoor exposure to pollutants. For basic or acidic compounds, these interactions are themselves influenced by surface pH and competition with other acidic or basic gases such as CO₂ and NH₃. We show that CO₂ tends to cause mineral surfaces to store more amines but NH₃ tends to decrease this surface capacity. Given the typical range of indoor CO₂ and NH₃ concentrations, the indoor sorptive capacity of amines on mineral surfaces may vary by greater than an order of magnitude.

Introduction

Sorptive interactions are important phenomena that can control indoor air concentrations and occupant exposure. Organic compounds, strongly adsorbed to indoor surfaces, tend to be released over a long time period into indoor air. Familiar examples include odors that linger after cooking or smoking. Indoor surface sorption kinetics and equilibria have been measured by many researchers (e.g. Colombo et al., 1993; Tichenor et al., 1991; Won et al., 2001), but little is known about the fundamental surface phenomena that control sorption on indoor surfaces. A mechanistic understanding of sorption to real indoor surfaces is an important, but formidable, goal as these surfaces are strikingly complex: mineral and organic, smooth and fleecy/porous, moist and coated with atmospheric deposits, greases and dirt. To initiate this inquiry, a relevant but simple mineral surface was evaluated.

Mineral surfaces are common, albeit low capacity, indoor adsorbents and some progress has been made in understanding sorption to these kinds of surfaces. Pennell et al. (1992) found that the vapor sorption of nonpolar organic compounds on hydrated soil and mineral surfaces can be explained as a multimechanistic process including (i) partitioning into organic matter, (ii) adsorption on mineral surfaces, (iii) dissolution into water films on the surface, and (iv) adsorption on surface-bound water. However, the degree of contribution of each process to sorption is dependent on many factors, including relative humidity (RH) which can strongly influence the sorptive capacity because of surface site competition or dissolution of polar organic compounds (Goss, 1992).

Although researchers have studied the influence of RH on the sorptive strength of volatile organic compounds on surfaces, it has only recently been recognized that pH and acid-base chemistry at indoor

surfaces may be important (Webb et al., 2002). The surface acidity can vary widely with changing indoor gas-phase concentrations of common indoor acidic and basic compounds such as ammonia, CO₂ and vinegar. Webb et al. (2002) studied the influence of ammonia on the adsorption of nicotine on indoor surfaces. They showed that the presence of gas-phase ammonia released by a cleaner can enhance the emission rate of nicotine from a carpet surface. Ammonia somehow modifies the surface, reducing its capacity for nicotine. They inferred that this may be due to an increase in the surface pH, thus driving protonated nicotine to its free-base, volatile form. We suggest that ammonia may instead compete with nicotine for surface sites (e.g. acid sites) and reduce the total surface capacity by taking up available sites.

Our broad goal is to develop a better understanding of indoor sorptive phenomena for acidic and basic organic pollutants such as volatile amines and carboxylic acids. The specific objective of this work is to identify surface phenomena governing the strength of sorption of a representative basic organic compound (trimethylamine, TMA) to a clean, mineral surface. A variety of surface interactions may contribute to observed adsorption phenomena including direct surface site adsorption and dissolution/acid-base chemistry in bulk surface water. However, to guide our experimental plan, we address two mutually exclusive hypotheses. Hypothesis 1: aqueous acid-base partitioning of the sorbate effectively stores a substantial amount of the organic base in bulk surface water and controls the overall sorptive capacity; thus the capacity is governed by the aqueous solubility, the pK_a of the sorbate and the pH of bulk surface water. Hypothesis 2: adsorption of an organic base is primarily a surface phenomenon, i.e. onto the solid surface or onto adsorbed water monolayers. A decrease in sorptive capacity for an amine in the presence of ammonia is because of competitive adsorption at the surface.

Conceptual model of organic sorption including acid-base chemistry

Surface water may act as bulk water at a high RH on mineral surfaces. Sumner et al. (2004) studied the interaction of water with various surface materials including quartz. Water uptake measurements, using infrared spectroscopy, showed that the surface water film on quartz exhibits spectra similar to bulk liquid water at 80% RH. Thus, overall surface capacity for a sorbate may be mediated by solution chemistry including absorption and acid-base chemistry (right side of Figure 1). As the RH decreases, disruptions in the hydrogen-bonded network and an increased interaction of the adsorbed water with the surface are observed (Sumner et al., 2004). As the RH decreases, bulk water phenomena should decrease and interactions with a different kind of surface may dominate.

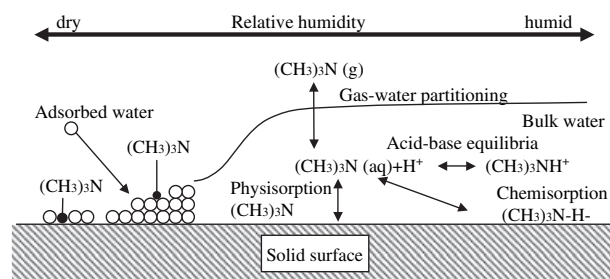


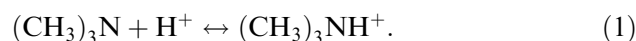
Fig. 1 Hypothetical trimethylamine interactions with dry surface, adsorbed water or bulk water

At mid-range RH values, several monolayers of adsorbed water may cover the surface and the species may adsorb preferentially onto the water layer (left side of Figure 1) (Goss, 1992; Ong and Lion, 1991). At low RH values, the adsorbate will compete with water for dry surface sites.

Hypothesis 1: dissolution and protonation in bulk surface water controls sorption

We assume here that when the RH is high, bulk water exists on surfaces. The sorptive capacity may then be dominated by dissolution of TMA and protonation in the water film. Given that bulk water is available at high RH, an organic amine is expected to interact with that water according to Henry's law and participate in aqueous acid-base chemistry. As the aqueous solubility of TMA is large, adsorption at the air–water interface is assumed to be insignificant compared with bulk aqueous phenomena.

Thus, gas-phase TMA ((CH₃)₃N_(g)) partitions to bulk surface water by Henry's law and aqueous TMA ((CH₃)₃N_(aq)) participates in acid-base equilibrium chemistry:



At the same time (CH₃)₃N_(aq) may physisorb to the surface ((CH₃)₃N_(surf)) or chemisorb to acidic surface sites ((CH₃)₃N–H_(surf)) (Boehm, 1966). At equilibrium then, the partition coefficient is:

$$k_e = \frac{\text{Mass of } \left[\begin{array}{l} (\text{CH}_3)_3\text{N}_{(\text{aq})} + (\text{CH}_3)_3\text{NH}^+ \\ (\text{CH}_3)_3\text{N}_{(\text{surf})} + (\text{CH}_3)_3\text{NH}_{(\text{surf})} \end{array} \right] \text{ per unit surface area}}{\text{Concentration of } (\text{CH}_3)_3\text{N}_{(\text{g})}}. \quad (2)$$

The relative influence of each form of TMA is uncertain, but all are likely to contribute to the overall adsorptive capacity of the surface. We assume here that k_e is controlled by the two aqueous species of the TMA acid-base equilibrium: neutral and protonated TMA. At a constant gas-phase concentration of TMA, (CH₃)₃N_(aq) is assumed to be constant by Henry's law, even if the pH of the water film changes. However,

$(\text{CH}_3)_3\text{NH}_{(\text{aq})}^+$ will increase with decreasing bulk water pH, around the $\text{p}K_a$ of TMA. The ratio of neutral to protonated TMA is given by:

$$\frac{[(\text{CH}_3)_3\text{N}_{(\text{aq})}]}{[(\text{CH}_3)_3\text{NH}_{(\text{aq})}^+]} = 10(\text{pH} - \text{p}K_a). \quad (3)$$

As the pH of the bulk surface water increases, as would be the case if the ammonia concentration increases in a room, the fraction of protonated TMA decreases substantially. Therefore, k_e should decrease exponentially over the pH region bracketing the $\text{p}K_a$ of the sorbate, and the sorbate will tend to partition to the gas (i.e. be emitted into the room). Defining k_e^0 equal to k_e where the pH of a water film is equal to the $\text{p}K_a$, the ratio of k_e/k_e^0 is given by:

$$\frac{k_e}{k_e^0} = \frac{1 + 10(\text{p}K_a - \text{pH})}{2}. \quad (4)$$

This dimensionless ratio is readily quantified experimentally and should increase exponentially as the pH drops below the $\text{p}K_a$ of TMA, if our hypothesis is valid. Otherwise, physisorption and chemisorption to the surface may dominate over dissolution and aqueous protonation.

A similar, but not identical, phenomenon may be observed if the surface is covered with acid sites and the amine preferentially chemisorbs to these sites. In this case, the effective surface $\text{p}K_H$ may also contribute to an observed increase in k_e as the pH of the bulk water decreases. To address this possibility, we titrated the surface to obtain $\text{p}K_H$ and acid site density on the surface (see Materials and methods).

Hypothesis 2: surface site adsorption controls observed sorption

Instead of dissolving into bulk surface water, an amine adheres to the surface, either by chemisorption or physisorption to dry surface sites or to adsorbed water. As a result, any influence of CO_2 or NH_3 on TMA adsorption is because of modification of the surface itself. We approach this hypothesis by testing two related phenomena: competitive adsorption (NH_3 and TMA) and isotherm analysis.

Active competition for surface sites may explain why ammonia influences surface capacity. Competitive adsorption is well characterized by Langmuir (Weber and DiGiano, 1996). The Langmuir isotherm, one of several well-known adsorption models, has been developed on the basis of dynamic equilibrium (Thomas and Crittenden, 1998). The isotherm assumes that adsorption occurs in one molecular layer of a sorbate on the surface with no interaction between sorbate molecules. Moreover, adsorption energy is assumed to be constant, i.e., the surface sites are homogenous. If multiple

sorbate species are present and the concentrations are high enough for the isotherm to exhibit non-linearity, the sorbates may compete for sites and disrupt their respective adsorption capacities. To apply an isotherm model which includes the effect of competition to experimental data, the model should be able to describe the adsorption of each compound over the concentration range of interest. Therefore, the Langmuir equation can be modified to predict the competitive adsorption among sorbates, where each sorbate independently follows the Langmuir isotherm. The Langmuir competitive adsorption, $q_{e,i}$ of the i th sorbate from an n -sorbate mixture is given by (Weber and DiGiano, 1996):

$$q_{e,i} = Q_{a,i}^0 b_i C_{e,i} \left(1 + \sum_{j=1}^n b_j C_{e,j} \right)^{-1}, \quad (5)$$

where q_e = amount of sorbate adsorbed per unit area of sorbent at equilibrium ($\mu\text{g}/\text{m}^2$); Q_a^0 = maximum adsorption capacity ($\mu\text{g}/\text{m}^2$); b = coefficient related to the net enthalpy of adsorption ($\text{m}^3/\mu\text{g}$); C_e = sorbate concentration at equilibrium ($\mu\text{g}/\text{m}^3$).

A substantial increase in the gas-phase concentration of any species j will decrease the surface capacity of competing species i . Thus, hypothetically, an increase in ammonia from using a cleaner decreased the surface capacity of nicotine on the carpet in Webb et al. (2002).

In testing this hypothesis, the effect of pH must be isolated. For example, increasing the gas-phase concentration of ammonia may indeed displace TMA, but it will also increase pH. By combining NH_3 and CO_2 , the pH can be controlled. Any pH-independent displacement of TMA is because of surface phenomena as NH_3 will not displace TMA in bulk water at a constant pH and temperature. Thus TMA sorption is a solid-surface phenomenon if we observe (i) pH-independent displacement of TMA, and (ii) predictive Langmuir competitive adsorption behavior.

Materials and methods

The sorbent chosen was zirconium silicate in the form of 0.18 cm diameter beads (Ceroglass, Inc., Columbia, TN, USA). This surface is representative of indoor materials such as window glass, or more porous mineral furnishings such as granite countertops, aggregate in concrete or mineral fibers in ceiling tiles. The beads were sonicated in distilled/deionized (DI) water for 30 min to remove impurities, and then baked in an oven at 60°C for at least 6 h prior to experimentation.

The sorbate chosen was TMA. TMA is mildly basic with a $\text{p}K_a$ of 9.8 and is functionally similar to nicotine with a $\text{p}K_2$ of 8.0 (Pankow et al., 1997). It is more volatile and less toxic than nicotine, and easier to work

with in experiments. TMA is also an important odorous air pollutant of indoor interest in its own right. It is commonly encountered as a nuisance odor from livestock operations (O'Neill and Phillips, 1992). At a pK_a of 9.8, significant changes in acid-base aqueous partitioning may occur in bulk surface water at realistic indoor ammonia concentrations.

Experimental apparatus

The evaluation of indoor surface sorption parameters is typically performed in a continuously mixed flow reactor style chamber (Won et al., 2001). These chambers provide environmental conditions and near-surface velocities that are comparable with those found indoors. However, the sorptive capacity of glassy surfaces is often at or below detection limits when measured in this configuration. To improve our ability to quantify sorptive capacity and distinguish among surface phenomena, we chose to measure the equilibrium partitioning in a plug flow reactor. This configuration allows us to increase the total silicate surface area in the reactor, increasing total adsorbed mass and reducing uncertainty in the measurements.

Shown in Figure 2 is a diagram of the experimental apparatus. The core component is a 50-cm Teflon reactor with an inner diameter of 1.8 cm for measuring sorption equilibria. The reactor is completely filled with zirconium silicate beads. TMA and water are simultaneously introduced into the system using a syringe pump. The solution is evaporated and diluted with high purity nitrogen (flow path A). The syringe pump delivers an aqueous TMA solution at a rate calculated to achieve a desired gas-phase concentration and RH at a total gas flow of 500 ml/min. For example a 630 mg/l solution of TMA in water delivered at a volumetric flowrate of 0.38 ml/h and diluted with nitrogen gas generates a gas-phase mixing ratio of 3 p.p.m. TMA at 50% RH and a total gas flow of 500 ml/min. Heat tape is wrapped around the tubing at the point of injection to help evaporate the TMA

solution into the system. Humidified nitrogen is delivered in a similar fashion in a separate gas line except that DI water was used instead of a TMA solution (flow path B). To adjust the pH of the aqueous surface film, gas-phase ammonia and CO_2 are delivered via a three-way Teflon solenoid valve to the total gas flow to achieve a desired pure-water equilibrium pH by Henry's law (Nazaroff and Alvarez-Cohen, 2001). The outlet gas is split into two streams: 50 and 450 ml/min. The 450 ml/min stream is delivered to a flask where pH, temperature, and RH are measured. We confirm the predicted pH of bulk surface water by sparging the exhaust air through 2-ml DI water via a gas dispersion frit (Ace Glass, Inc., Vineland, NJ, USA) and measuring the pH of that water using a pH probe. Note that the *reported* pH is calculated based on Henry's law and acid-base equilibria; the primary purpose of the pH measurement is to ensure that the experimental system is working properly. Because of small losses in the system, an actual flow of 40 ml/min is delivered to a continuous analyzer for quantification. All experiments are conducted at 25°C and the internal pressure of the Teflon reactor is 1.1 atm.

For experiments conducted at a gas-phase mixing ratio ≥ 1 p.p.m. TMA, we use a flame ionization detector (FID) with a detector temperature of 250°C. For experiments conducted at 50 and 100 p.p.b., a chemical ionization mass spectrometer (CIMS) is used. In our CIMS system, we employ a proton transfer reaction using protonated water as a reagent ion to ionize TMA molecules (Španěl and Smith, 1998). Protonated TMA is then detected by a quadruple mass spectrometer (ABB Extrel, Inc., Pittsburgh, PA, USA). The FID and pH meter are connected to a data acquisition system in which the data were directly stored in the computer, while the temperature and RH were recorded manually.

For ammonia sorption experiments, we use a sample-draw transmitter (Thermo Gas Tech, Inc., Newark, CA, USA) to detect and quantify ammonia. The instrument has its own pump and requires an airflow

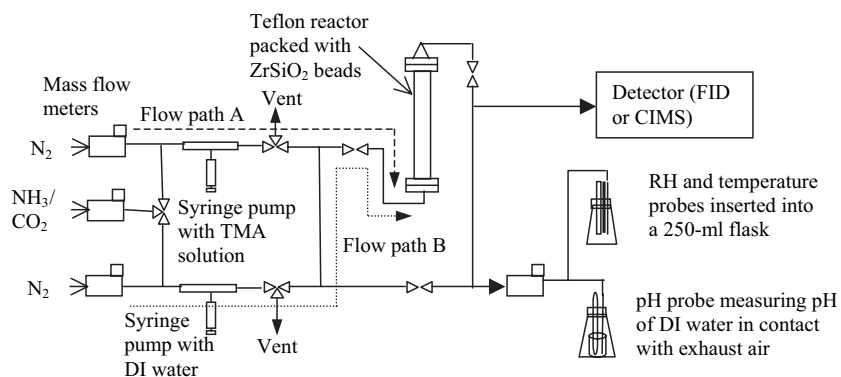


Fig. 2 Experimental apparatus. Aqueous trimethylamine (TMA) is vaporized, diluted and delivered via flow path A to a Teflon plug-flow style reactor packed with zirconium silicate beads. Equilibrium adsorption partition coefficient derived from breakthrough experiments

rate of 280 ml/min. The remaining flow is directed to a flask where pH, RH, and temperature are measured.

Experimental procedures

Clean humidified nitrogen (flow path B) is first supplied to the reactor until the desired RH, measured at the exhaust, is reached. Subsequently, a sorption stage is initiated by introducing gas-phase TMA to the reactor (flow path A) while at the same time directing the clean humidified nitrogen to a vent. This stage typically requires approximately 1 h to achieve equilibrium but is allowed to run for an additional 30 min to obtain an average signal value for gas calibration. The humidified nitrogen is then redirected to the reactor (flow path B) while the gas-phase TMA is redirected to a vent. This desorption stage also requires about 1 h. The k_e value is determined from total mass of TMA accumulated per unit surface area divided by inlet sorbate concentration. By convention for indoor materials, k_e is referenced to the geometric surface area, not the total surface area (i.e. internal pore area). To quantify the total mass accumulated, we apply the trapezoid rule to calculate the sorption area which excludes the pre-determined lag time of the system and we then convert this sorption area to mass using a two-point calibration on either the FID or CIMS as appropriate. The reactor lag time was determined by performing a pulse residence time distribution using propane as a conservative tracer.

The isotherm experiments were conducted at 20, 50, and 90% RH and at five different TMA inlet mixing ratios of 0.1, 1, 2, 3, and 6 p.p.m. At 50% RH, 50 p.p.b. TMA was additionally studied. To determine the influence of the surface pH on k_e values, the experiments were conducted at three RH conditions but only 3 p.p.m. TMA was used. Ammonia and CO₂ gases were added at the inlet flow to obtain a desired pure-water equilibrium pH, varying from 8 to 11 which covered a pH region around a TMA pK_a of 9.81.

To test the hypothesis that ammonia displaces TMA at surface sites, regardless of the water-film pH, we performed two experiments at the identical pH value. In the first, only TMA was present (from an isotherm experiment). In the second, TMA, NH₃ and CO₂ were all present but the inferred surface water-film pH (pH = 9.6) was the same as for the previous experiment. We conducted a sorption experiment at 50% RH and TMA mixing ratio of 3 p.p.m. by maintaining gas-phase ammonia at 800 p.p.m. Carbon dioxide at 200 p.p.m. was also added to maintain the pH of the water film constant to ensure that the influence of ammonia on k_e was independent of a change of the pH. Clean humidified nitrogen along with ammonia and CO₂ were initially supplied to the reactor until the RH reached 50%, then gas-phase TMA was introduced.

Quantification of surface acid sites, surface area and pore distribution

To better understand the sorptive behavior of TMA, we have further studied the surface physical/chemical characteristics of the zirconium silicate beads used in this work. The acid site density, Γ_m , (mol/g of solid) and acidity constant, pK_H , of the surface were determined using a batch equilibrium acidimetric-alkaline titration method developed by Wang et al. (2000). We used a solid-to-liquid ratio of 50 g of beads to 100 ml of 0.01 M NaNO₃ solution. Accessible surface area and pore volume distribution were determined using N₂ Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halendar (BJH) desorption analyses.

Bulk water equilibrium pH in contact with residential air

As bulk water surface pH is an important variable in this study, we measured the pH of purified water in contact with air in residences. We sought to (i) obtain 'typical values' and (ii) determine whether the measured levels of indoor CO₂ and NH₃ are sufficient to predict bulk water pH. We measured the pH using a method similar to that used in the sorption experiment. A sampling pump (MSA Co., Pittsburgh, PA, USA) was used to draw ambient air at a rate of 2 l/min through 25-ml DI water. A pH probe was installed in the water and the pH was measured at 5-min intervals for 30 min. We report the final pH values here. While measuring the pH, we also measured the concentrations of NH₃ and CO₂ as well as the RH using a photoacoustic multi-gas monitor (Brüel & Kjær, Inc., Nærum, Denmark). One set of pH measurements was conducted in a kitchen while a commercial liquid ammonia (~10%) cleaner was applied to the floor. The occupant washed the kitchen floor using a sponge soaked with ammonia cleaner for 20 min. The experiment was carried out in residence occupied by two people, two dogs and one cat.

Results

Bulk water pH, TMA pK_a and dissolution do not explain adsorption behavior

Figure 3 shows anticipated and experimental responses of k_e as the pH of hypothetical bulk surface water is modified by adding either gas-phase ammonia or CO₂. In this figure, the partition coefficient is normalized by the value measured at pH = 9.8 (the pK_a of TMA). The model curve was derived from Equation 3. The experimental results shown were carried out at 90% RH to ensure that some bulk surface water is present.

If only aqueous chemistry in the bulk surface water influences overall adsorption, the model predicts a substantial increase in the ratio of k_e/k_e^0 as the pH decreases. However, this ratio only increases modestly

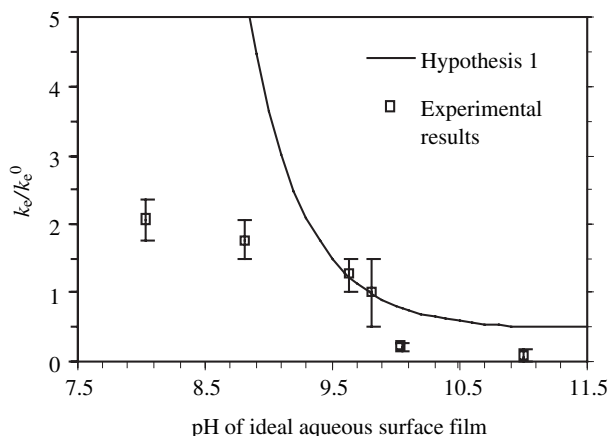


Fig. 3 Normalized experimental equilibrium partition coefficient, k_e/k_e^0 as the surface pH is modified by either gas-phase ammonia or CO_2 . Also shown is the hypothesis 1 model prediction considering dissolution and acid-base aqueous chemistry in bulk surface water. Uncertainty range shown is based on error propagation of the standard error from replicate experiments

as the pH of bulk water on the surface is decreased by contacting the surface with CO_2 at 28 and 1000 p.p.m., corresponding to water pH of 8.8 and 8.0 respectively. We note that an inflection point occurs between pH 9.6 and 10. This occurs at about the $\text{p}K_a$ of TMA, but also occurs where ammonia is added to raise the pH.

RH, CO_2 , and NH_3 influence partition coefficient

Figure 4 shows the relationship between k_e and RH at various inlet mixing ratios. The decline of the k_e values with increasing the RH or the amount of surface water is observed at all inlet mixing ratios, especially at a lowest mixing ratio of 0.1 p.p.m. The results for TMA at 0.1 p.p.m. exhibits unusual behavior as the k_e value at 20% RH is reproducibly much higher (0.22 m) than anticipated given trends for 2 p.p.m. TMA and greater. A similar, but more modest, inflection is observed for the 1 p.p.m. results, where the partition coefficient at 20% RH is somewhat higher than would be anticipated given the results at higher TMA mixing ratios.

Carbon dioxide and ammonia appear to significantly modify the adsorptive surface capacity for TMA as shown in Figure 5. For CO_2 an increase in k_e values was observed for all RH values from dry to humid. Even a modest mixing ratio (28 p.p.m.) of CO_2 appears to enhance the sorption coefficient at 90% RH. At a realistic CO_2 mixing ratio (1000 p.p.m.), we observe a moderate increase in the surface capacity for TMA at all RH values. At 90% RH, where bulk surface water may reasonably be assumed to exist, CO_2 has the effect of increasing the surface capacity for TMA by $\sim 60\%$. For a modest mixing ratio of NH_3 (10 p.p.m.), the TMA capacity decreases a small amount at low RH, but k_e decreases by a factor of 2 and 6 at 50 and 90% RH

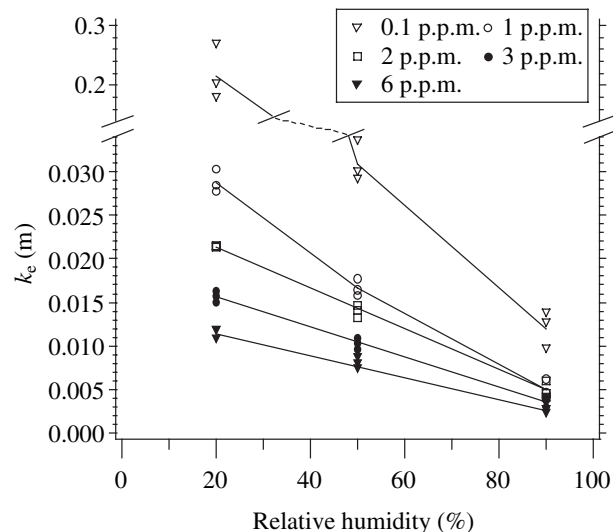


Fig. 4 Relationship between RH and k_e for trimethylamine mixing ratios ranging from 0.1 to 6 p.p.m.

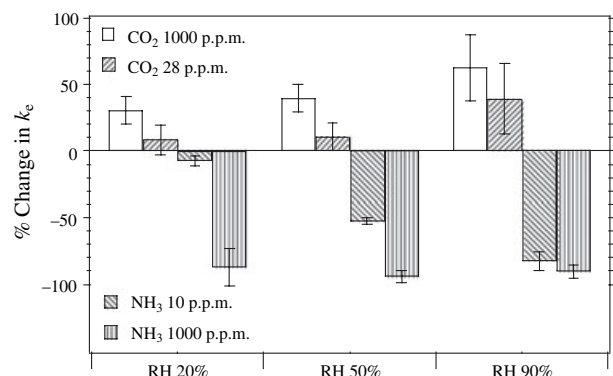


Fig. 5 Percentage change in the equilibrium partition coefficient, k_e , at 20, 50 and 90% RH due to the presence of CO_2 or ammonia; the trimethylamine mixing ratio is held at 3 p.p.m. Uncertainty range shown is based on error propagation of the standard error from replicate experiments

respectively. At a very high mixing ratio of NH_3 (1000 p.p.m.) the surface capacity for TMA is almost completely depleted and k_e is reduced by a factor of 8–20.

TMA follows Langmuir isotherm and competitive adsorption with NH_3 is observed

To explore the possibility that amines preferentially sorb to the solid surface (instead of bulk surface water), we evaluated the surface capacity over a wide range of gas concentrations. We also evaluated the equilibrium adsorption behavior of ammonia. For both species, we observe nonlinear sorption isotherms as illustrated in Figure 6. At each RH value, the isotherm appears to follow the Langmuir model, where sorptive capacity decreases at higher concentrations because fewer surface sites are available for sorption. At the highest TMA concentration, we observe a distinct increase in capacity that deviates from the Langmuir model. The

Table 1 Langmuir constants and partition coefficients for TMA and NH₃

Sorbate	% RH	Q_a^0 ($\mu\text{g}/\text{m}^2$)	b ($\text{m}^3/\mu\text{g}$)	k_e (m)
TMA	20	200 ^a	2.2×10^{-4a}	0.043 ^a
	50	98	3.2×10^{-4}	0.031
	90	29	4.5×10^{-4}	0.013
NH ₃	50	196	2.2×10^{-4}	0.043

^aThese values are based on isotherm data that excludes 0.1 p.p.m. TMA.

single-sorbate isotherms of TMA at 20, 50, and 90% RH along with ammonia at 50% are fit to the Langmuir isotherm with R^2 equal to 0.97, 0.99, 0.95, and 0.91 respectively. Table 1 shows the Langmuir constants (from Equation 5), Q_a^0 , b , and k_e values obtained from a multiple of Q_a^0 and b for the linear, low concentration, range of the Langmuir isotherm.

To develop a competitive adsorption model, we apply the Langmuir-type competitive model, (Equation 5) to experimental observations of pure species isotherms, as each gaseous compound (TMA and ammonia) exhibits Langmuir isotherms up to a gas phase TMA mixing ratio of 3 p.p.m. (Figure 6). Calibrating with isotherm parameters derived from pure species isotherms (Table 1, 50% RH), we should be able to predict the surface capacity for TMA in the presence of NH₃ if the competitive hypothesis is correct. To verify the model, we conducted TMA sorption experiments at 3 p.p.m. with ammonia mixing ratios of 10, 20, and 40 p.p.m. The experiments were also conducted at 50% RH. As shown in Figure 7, the calibrated model adequately describes TMA adsorption influenced by gas-phase ammonia at 50% RH.

To demonstrate that ammonia competes with TMA for surface sites in the absence of pH change, the equilibrium surface capacity was determined for two different ammonia concentration levels as described in the Materials and methods section. Recall that CO₂

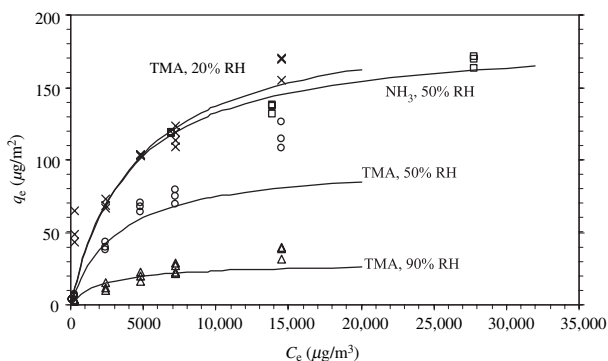


Fig. 6 Predicted sorption isotherms (parameters fit to Equation 5 for single species sorption) of ammonia and trimethylamine (TMA) at various relative humidity (RH) values at 25°C (solid lines) and experimental results; × for TMA at 20% RH, ○ for TMA at 50% RH, Δ for TMA at 90% RH, and □ for NH₃ at 50% RH

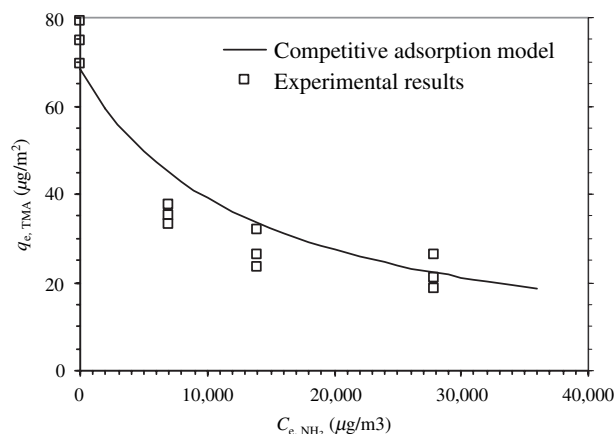


Fig. 7 Predicted competitive adsorption and experimental results obtained from TMA sorption experiments that include ammonia at mixing ratios of 10, 20, and 40 p.p.m.

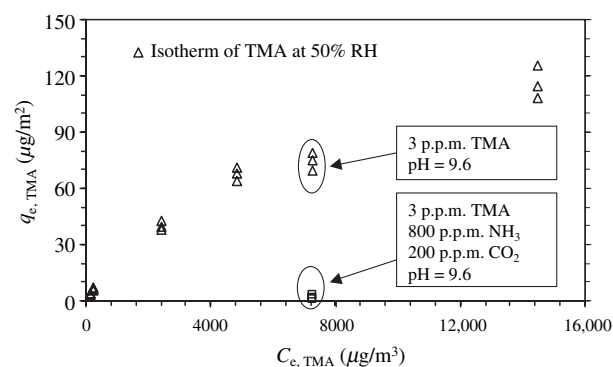


Fig. 8 The sorptive capacity of TMA in the presence of 800-p.p.m. NH₃ and 200-p.p.m. CO₂ (□) compared with the capacity without NH₃ (Δ) at 50% RH

was used to ensure that any bulk water remained at the same pH (9.6). The 50% RH isotherm for TMA, in the absence of NH₃, is reproduced in Figure 8. This isotherm can then be compared with a set of results obtained at an ammonia mixing ratio of 800 p.p.m. The equilibrium capacity of TMA sorbed on the surface was decreased by a factor of 40 in the presence of ammonia. This pH-independent decrease in capacity suggests that ammonia and TMA are competing for surface sites.

Surface acid site characterization

Figure 9 shows the result of a net titration for the zirconium silicate beads using the method of Wang et al. (2000). The surface contains three types of acid sites. Their pK_H are 2.5, 6.5, and 11.0 with the surface sites per unit area of 1.8×10^{-5} , 2.4×10^{-6} , and 6.3×10^{-6} mol/m² respectively (based on N₂ BET surface area). Surface area accessible to N₂ by BET analysis was 0.16 m²/g, roughly 300 times greater than the superficial area of the beads of 0.00054 m²/g.

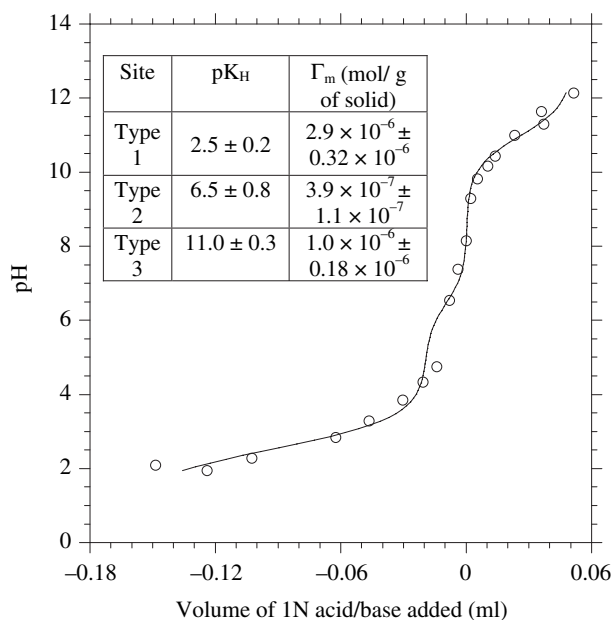


Fig. 9 Titration result for zirconium silicate beads using a solid-to-liquid ratio of 1:2 and ionic strength of 0.01 M NaNO₃

Bulk water equilibrium pH ~5.2 in contact with residential air

Table 2 shows the final pH values, mean values of mixing ratios of CO₂ and ammonia, and RH measured in five residences between November 22 and December 5 2004. These compare well with reported range of residential ammonia and CO₂ mixing ratios of 1–60 p.p.b. (Atkins and Lee, 1993; Brauer et al., 1991; Suh et al., 1994) and 300–3500 p.p.m. (Seppänen et al., 1999) respectively. The measured pH values in this study range from 5.0 to 5.2 which are somewhat lower than the predicted values determined on the basis of Henry's law and acidity constants of CO₂ and ammonia gases. This may be because of the presence of other acidic gases (Brauer et al., 1991) that could lower the pH such as nitric acid, carboxylic acids, etc. In these apartments, the CO₂ concentrations were at about the anticipated level for modest ventilation rates during winter.

We also measured the equilibrium water pH while the occupant washed the kitchen floor with an ammonia cleaner. The measured pH and ammonia mixing

Table 2 The equilibrium pH of water in contact with air, mixing ratios of CO₂ and ammonia, and relative humidity in five residences

Apartment no.	pH		Mean value		
	Measured	Predicted	CO ₂ (p.p.m.)	NH ₃ (p.p.m.)	RH (%)
1	5.2	5.4	870	<0.2	50
2	5.2	5.6	510	<0.2	48
3	5.1	5.5	670	<0.2	31
4	5.2	5.6	500	<0.2	26
5	5.0	5.5	710	<0.2	45

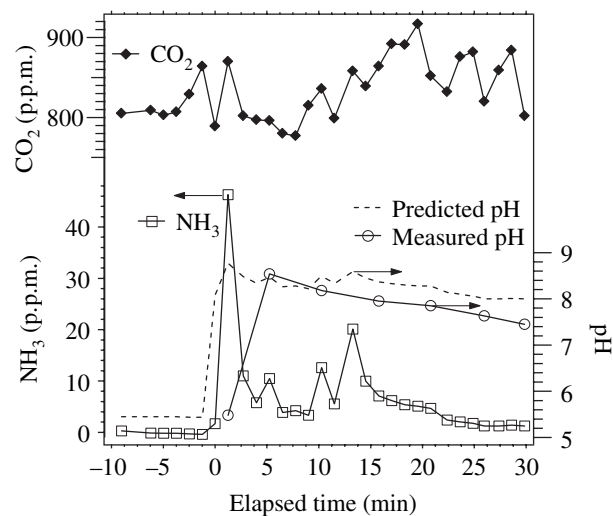


Fig. 10 Measurements of the pH, CO₂ and NH₃ as an ammonia cleaner was applied to a kitchen floor. Also shown is the predicted pH for equilibrium CO₂ and NH₃ partitioning into water

ratio are shown in Figure 10. The average mixing ratio of CO₂ was 840 p.p.m. and RH was 52% during the experiment. As the ammonia cleaner (pure solution from the bottle) was introduced, the ammonia mixing ratio increased to 46 p.p.m. and the pH increased to 8.5, which is in agreement with the predicted value of 8.7. With time, the ammonia concentration decreases by ventilation, and perhaps deposition, and the pH decreases.

Discussion

Broadly, our results point away from hypothesis 1 (bulk surface water and solution chemistry) and toward hypothesis 2 (surface interactions). Several lines of evidence argue against bulk water chemistry driving sorption. However, some observations suggest that acid-base chemistry in bulk water contributes in a modest way to the overall surface capacity for TMA.

Evidence against bulk water chemistry controlling adsorption

The first indication that bulk water chemistry is less important in sorption is that the sorption behavior as pH changes does not match model behavior predicted by hypothesis 1 as shown in Figure 3. Instead of an exponential decrease in surface capacity as pH increases, we observe an inverted S-shaped curve with a strong inflection at the point where ammonia is introduced. This poor fit of the experimental results with the predicted model suggests that a change of surface water film pH is not a key parameter that governs the vapor sorption of TMA on the hydrated zirconium silicate surface.

Further evidence against hypothesis 1 comes from the RH results. The TMA surface capacity is observed to decrease in Figure 4 at all TMA mixing ratios as RH

increases. Given that Sumner et al. (2004) found that bulk water exists above 80% RH on mineral surfaces, we would anticipate that increasing RH from 50 to 90% RH will result in a significant increase in the total volume of bulk water on the surface. In this case, more water means more TMA adsorption capacity by dissolution. Instead, we observe a decrease in overall surface capacity for TMA as RH increases.

Evidence for solid surface/hydrated surface adsorption

Solid surface or air–water interfacial interactions appear to overwhelm any increase in TMA absorption/dissolution capacity in the bulk water. Sumner et al. (2004) characterized the hydrated glass surface using atomic force microscopy and found that water does not completely cover the surfaces even at RH above 60%. Instead, the surfaces are covered with water islands. However, the relationship between the fraction of the surfaces covered with such water islands and the RH was not studied, only equivalent number of water monolayers were reported. Therefore, at moderate to high RH conditions, TMA may simultaneously be bonded to dry surface, adsorbed water molecules and dissolved into bulk water.

Our humidity-dependent adsorption results echo those of Goss (1992). Goss studied the sorptive capacity of 17 polar and nonpolar organic compounds on quartz sand at RH ranging from 10 to 90%. Goss found that k_e values decrease with increasing RH. Below 26% RH, equivalent to one molecular layer of adsorbed water, adsorption of organic molecules on free water surface sites is an important sorption mechanism, while adsorption on the surface coated by a complete water film becomes dominant as the RH increases above 26%. Goss also suggested that competitive adsorption between organic and water molecules contributes to a decrease in k_e in the RH region below 26% as water molecules are preferentially adsorbed on the mineral surface. In addition, the Goss study of heats of sorptions at 30–70% RH showed that the polar sorbents containing oxygen atoms have higher heats of sorptions than their heats of condensation. This was explained by an increase in binding forces between the hydrogen of the water and the electron donors of the sorbates at the liquid–gas interface. Thus, instead of competition for dry surface sites between TMA and water, we may be observing progressively weaker binding of TMA to sorbed water molecules as the number of monolayers increases with RH.

Similar behavior was observed in a study of gas-phase trichloroethylene (TCE) sorption to soil minerals. Based on their results, Ong and Lion (1991) proposed sorption processes corresponding to three regions. (i) Below one monolayer of adsorbed water, the observations based on heats of sorption were similar to Goss' (1992) study. Direct vapor adsorption

on the solid surface and competition with water molecules were indicated. (ii) Between one and five layers of water coverage, the sorption was attributed to adsorption of TCE onto surface-bound water rather than dissolution into adsorbed water. The dissolution limitation may be due to a modification of the first several layers of adsorbed water by interaction with the mineral surface. Ong and Lion did not observe competition between water and sorbate molecules for sorption in this region. We may tentatively conclude that TMA competition with water molecules for dry surface sites at 50% RH contributes to sorption in a minor way. (iii) Above five layers of adsorbed water, dissolution of TCE into condensed water and partitioning at the solid–liquid interface become dominant.

Considering these findings and our results, dissolution into adsorbed bulk water is probably not the major contributor to the sorption of TMA even at 90% RH where surface water is expected to behave like bulk water. However, without experimental results at 0% RH, we may not conclude that adsorption on the water-free surface is the dominant sorption mechanism. At low humidity and low TMA concentrations, we observed that ZrSiO₂ surface had an unusually high capacity for TMA (Figure 4). Goss (1992) also observed unusually high k_e values for organics on mineral surfaces at humidities below 26%. It is unclear why this phenomenon was not observed for TMA at mixing ratios > 1 p.p.m. However, this suggests that measurements of sorption characteristics for polar, acidic or basic compounds should continue to be carried out at mixing ratios relevant to indoor conditions, e.g., in the p.p.b. range for most organics.

CO₂ and NH₃ modify the adsorptive surface capacity for TMA

While we conclude that aqueous chemistry in bulk water is not the major contributor to sorbent capacity, we do observe phenomena that point to acidification of either the dry solid surface, surface bound water or bulk water. Figure 5 demonstrates that CO₂ tends to increase the sorbent capacity of TMA at all RH. Comparing the trends in k_e (Figures 4 and 5) as RH increases, we observe that CO₂ has the effect of offsetting the water-induced reduction in TMA capacity. At 20 and 50% RH, an increase in k_e may be explained by an acidification of the surface-bound water by CO₂, thus increasing the availability of acidic sites. At 90% RH, an increase in k_e may also be due to an increase in protonated TMA as the adsorbed bulk water has become more acidic. In addition, TMA dissolved in the bulk water could chemisorb onto solid surface sites made increasingly acidic by CO₂. Conversely, NH₃ may deplete acid sites. The depleting influence of NH₃ appears to be enhanced by increasing RH, possibly indicating that aqueous phenomena are still important.

As shown in Figure 3, an inflection point occurs as gas-phase ammonia is used to increase the pH of the water film. As we have concluded that dissolution of TMA into bulk liquid water on the surface is not the key sorption mechanism, we hypothesize that the significant reduction in the surface capacity for TMA is attributed to a competition between TMA and ammonia molecules for surface sites. The isotherm measurements shown in Figure 6 are clearly nonlinear and appear to fit the Langmuir model (see Table 1). Combining independently derived Langmuir coefficients we show in Figure 7 that the reduction in the partition coefficient, in the presence of ammonia, is predictable. Combined, these results point strongly to surface sorption (either dry or adsorbed water) with competition for sites between TMA and NH_3 . Even if the hypothetical surface water pH is held constant, we show in Figure 8 that NH_3 clearly displaces TMA. We note that the sorbent capacity results at a high TMA concentration appear to deviate from the Langmuir model. This is probably due to the formation of multiple layers of TMA at the high relative pressure of the sorbate.

Our analyses of surface acid sites yields some clues about sorption mechanisms. We determined surface $\text{p}K_a$ values at 2.5, 6.5, and 11. At these $\text{p}K_a$ values we would anticipate a significant shift in surface acid site density. Within our design pH range (8–11) of bulk surface water, we would anticipate a change in available acid sites by about a factor of two. If chemisorption is an important mechanism, this could explain some of the decrease in surface capacity as pH increases. As NH_3 appears to participate in competitive adsorption with TMA, the pH range between 8 and 9.6 is more useful. In this range, only CO_2 is used to adjust acidity. From pH 8 to 9.6, surface acid site density should decrease by about 14%. This may contribute to a portion of the observed 40% increase in TMA capacity. A caveat: given that the nature of the water on the surface is unknown, applying the concept of pH the bound surface water may be unrealistic.

Solid surface acid sites account for small fraction of TMA capacity

Acid site density is consistent with surface area measurements, but not with TMA coverage. The acid sites with $\text{p}K_H = 11$ are of interest in this research as we have studied the influence of the surface pH ranging between 8 and 11. Based on BET surface area measurements, the surface concentration of acid sites is $6.3 \times 10^{-6} \text{ mol/m}^2$, corresponding to a site area of $2.6 \times 10^{-15} \text{ cm}^2$ per site. This corresponds to a reasonable site diameter of roughly 5 Å. The highest predicted TMA coverage based on isotherms is much smaller than anticipated if driven primarily by density of acid sites. Given a density of liquid TMA of 0.657 g/cm^3

(Matheson Company Inc., 1961), the cross-sectional area of one TMA molecule is $3.4 \times 10^{-15} \text{ cm}^2$ (or $4.9 \times 10^{-6} \text{ mol/m}^2$). This area closely corresponds to the acid site area. However, the maximum adsorption capacity at 20% RH ($\sim 1.1 \times 10^{-8} \text{ mol/m}^2$) is only small fraction of the measured acid site density. Interestingly, surface coverage of TMA at low humidity corresponds more closely to the superficial geometric surface area of the beads. Pore size distribution analysis showed that most pores are 20 Å or greater in diameter and that most internal porosity should be available to TMA.

Partition coefficient smaller than that observed for other indoor surface organic interactions

The k_e values obtained for our glassy surface (mostly lying between 0.003 and 0.04 m) are somewhat higher than that reported by Goss (1992) for a variety of polar and nonpolar organic species on quartz (ranging from 10^{-6} to 10^{-4} m). Referencing our k_e results to the BET surface area ($k_{e,\text{BET}}$ ranges from 10^{-5} to 10^{-4} m) instead of the geometric area results in a better correspondence with Goss. Our results are much lower than values reported by other researchers which typically lie between 0.1 and 5 m for indoor surfaces (Tichenor et al., 1991; Won et al., 2001). Unfortunately, indoor surface researchers were unable to quantify k_e on glass because of low sorption strength and limitations of their equipment (Tichenor et al., 1991). The closest material for comparison would be ceiling tiles which are composed of mineral fibers. The values reported are about 5–10 times greater for TCE than our values for TMA. However, the basis of k_e is the superficial planar area of the ceiling tile while our values are based on the superficial surface area of individual beads. Furthermore, ceiling tiles are often painted and TMA was not tested as a sorbate. For these reasons, we find it difficult to compare our k_e values with those determined on other indoor materials.

Conclusions

These experiments demonstrate that dissolution into bulk surface water along with acid-base chemistry on the surface is not the major sorption process for a representative amine on a mineral surface. However, CO_2 contributes to a modest increase in k_e . CO_2 may acidify the surface-bound water, thereby increasing the number of available acid sites. Unlike the influence of CO_2 on k_e , gas-phase ammonia reduces the sorptive strength substantially. This phenomenon is explained by a competition between ammonia and TMA molecules for adsorption sites. The adsorption isotherms reasonably fit the Langmuir competitive model.

Development of equilibrium adsorption isotherms and kinetic parameters in the absence of the appropriate levels of sorbate, water, CO₂ or NH₃ can lead to unreliable results. Other acidic or basic gases and aerosols are present indoors (Brauer et al., 1991) and may also become important in understanding adsorption. Nonlinear sorption for TMA at levels as low as 1 p.p.m. suggests that future research on the sorption of similar species cannot rely on an assumed linear isotherm. Because of the difficulty in detecting species such as TMA and nicotine, researchers may be tempted to use high concentrations for convenience. However, adsorption isotherms representative of indoor TMA concentrations must be performed at gas-phase concentrations significantly < 1 p.p.m., and preferably in the appropriate range for that species in typical indoor settings. To our knowledge, this is the first example of enhanced sorptive capacity of indoor materials due to CO₂. Because of its ubiquity and variability in indoor environments, it is especially important for future adsorption research on acidic or basic compounds to include CO₂ in the diluent gas.

In considering the impact these findings have on understanding indoor air quality, we recognize that glassy surfaces are generally low-capacity sorbents unlike carpet or painted walls. However, this research should help guide research on more complex indoor surfaces. For example, if bulk water exists on painted wall board at moderate to high RH, then the capacity for basic compounds should increase with increasing CO₂. Given the functional similarity between ammonia and organic amines, we anticipate that these compounds will participate in competitive adsorption if suitable acidic surface sites exist, regardless of surface.

As typified by our residential experiments and prior research (Atkins and Lee, 1993; Brauer et al., 1991; Seppänen et al., 1999), 'normal' indoor conditions roughly correspond to mixing ratios for CO₂ and NH₃ of > 500 and < 0.2 p.p.m. respectively. Generally, we would expect amine and ammonia levels to be low enough that their respective adsorption isotherms will fall in the linear range. Therefore, competitive adsorption should not be a major factor influencing surface

capacity. In this case, any pH-driven changes (e.g. by CO₂) may indeed become more important, in a relative sense. However, sharp increases in ammonia from cleaning (Figure 10) or from animal/human wastes are common and clearly increase the NH₃ concentration into a non-linear adsorption regime. These events are certain to drive amines off mineral surfaces, by the mechanism of competitive adsorption, and into the breathing zone. Considering Webb et al. (2002) results in this light, the pH change due to an ammonia cleaning episode is more than enough to shift the acid-base partitioning of nicotine ($pK_a = 8$) in a water film, but is not sufficient to shift the acid-base partitioning of TMA ($pK_a = 9.8$). Competitive adsorption may also explain the observation that nicotine desorbs rapidly in the presence of ammonia. Yet, structural differences between TMA and nicotine, and differences among surfaces tested make any conclusive comparisons between these systems premature.

The next steps are clear. We must evaluate the adsorption equilibria and kinetics for the more complex surfaces that are so ubiquitous in indoor environments such as carpet and paint. In addition, we need to expand the suite of sorbates to include other amines and acids. We have begun evaluating these equilibrium phenomena with painted surfaces. However, we are finding that paint exhibits behavior that is very different from the zirconium silicate beads. Therefore, we emphasize that the results from the present research is relevant to mineral surfaces only.

Acknowledgements

We thank the University of Missouri Research Board for supporting this work. We also thank Dr Jianmin Wang and Tian Wang of the University of Missouri-Rolla (UMR) for advice on a batch titration experiment, Dr Douglas Ludlow of UMR for performing N₂ BET analyses and Drs Brett Singer and William Nazaroff of Lawrence Berkeley National Laboratory and U.C. Berkeley for advice and technical assistance. This material is based upon work supported by the National Science Foundation under Grant No. 0238721.

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