

# Sorption Phenomena of Nicotine and Ethenylpyridine Vapors on Different Materials in a Test Chamber

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The sorption phenomena that nicotine undergoes in indoor environments are generally recognized as a limitation in its use as a marker for environmental tobacco smoke (ETS). An empirical description of these phenomena is proposed, and they are compared to those exhibited by a well-accepted ETS gas-phase marker, ethenylpyridine. The sorption of both compounds onto different surfaces (glass, cotton, and nylon fabrics) was investigated through dynamic experiments in a 1-m<sup>3</sup> glass chamber. The combined influence of the nature of the sink and of relative humidity on the sorption of each compound is outlined. These results can be used to predict the dynamics and the magnitude of these processes. As much as 1 mg of nicotine can be adsorbed and re-emitted from 1 m<sup>2</sup> of cotton cloth over a few hours, and consequently the significant biases likely to be caused if nicotine is used to assess low-level ETS exposures need to be addressed. These could arise from re-emission of adsorbed nicotine from indoor surfaces after the air would have been cleared of ETS, or from its transport on clothing and subsequent re-emission.

## Introduction

Nicotine, the major tobacco alkaloid, is the most widely used chemical marker for the assessment of exposure to environmental tobacco smoke (ETS) (1). This is because, although it is not unique to tobacco, its presence in indoor air is generally assumed to be the specific result of the combustion of tobacco. In ETS, nicotine is almost totally found in the gas phase (2) and can therefore rapidly diffuse to surfaces with which it will interact (3, 4). The importance of this effect has been given as the reason for the poor correlation that is often observed between nicotine levels and the concentrations of other ETS constituents in indoor environments (5). Using 3-ethenylpyridine, a pyrolytic decomposition product of nicotine, as an ETS marker has been advocated because while being as specific as nicotine, it does not appear to be affected by sorption to the same extent (6, 7).

The present study was aimed at proposing an empirical model describing the dynamics of nicotine sorption and at quantitatively assessing it. Nicotine sorption was compared to that of ethenylpyridine (EP) by simultaneously assaying both compounds, and the impact of sorption phenomena on the validity of nicotine use as a marker could thus also be assessed.

The impact of sink phenomena on indoor air quality is becoming of increasing concern (8, 9). In the past two

decades, numerous studies have addressed the effect of sorption on the dispersal of indoor air pollutants. Most of them, e.g. refs 10 and 11, were restricted to VOCs, although early studies had shown much larger sorption effects from less volatile compounds (12, 13). Few quantitative studies have systematically addressed the sorption dynamics of pollutants onto materials, investigating both an uptake and a degassing phase (14, 15). Two teams have reported on nicotine sorption in test chambers. The first studied its uptake by human hair (16), and the other addressed the modeling of its sorption in a steel chamber (17, 18). Both studies involved rather large concentrations, however, and the latter's design was such that short-term dynamics could not be effectively investigated.

## Experimental Section

**Equipment and Experimental Procedures.** The experimental conditions were so designed that results would be directly applicable to normal levels of nicotine in indoor environments, focusing on rather short-term events. Thus dynamic studies with a maximal duration of a few days were performed, operating as recommended in ref 19.

**Experimental Chamber.** A cubic 1-m<sup>3</sup> glass chamber with Teflon ports was operated under positive pressure (metering all flows pumped into it). The chamber was supplied with filtered, active carbon purified air so as to maintain a preset air exchange rate. Relative humidity (RH) was controlled and regulated ( $\pm 3\%$ ). The room temperature remained constant at  $23 \pm 1^\circ\text{C}$ . Temperature, RH, and all flows were logged continuously. Two Teflon-coated fans assured the air mixing (homogeneity was checked using CO as a tracer). The air speed 1 cm above the bottom surface was between 5 and 15 cm/s and found to be fairly turbulent. This is well within the range recommended for up-scaling to rooms the results from small chambers (20).

**Reagents and Analytical Determinations.** Nicotine [54-11-5] was obtained from Sigma. The 3-isomer of EP, prevailing in ETS (6), was not commercially available and most tests were done using 4-ethenylpyridine [100-43-6] (Sigma). Some experiments were carried out using 3-ethenylpyridine [1121-55-7], synthesized according to ref 21. No difference was found between the results obtained with either the 3- or the 4-isomers.

Nicotine and EP were simultaneously sampled on XAD4 (10 min at 1.5 L/min) and quantified by GC (22). To avoid losses to the line, the glass sampling tubes were extended into the chamber at the end of a rigid Teflon tube. Sink samples were extracted, immediately after their collection, with ethyl acetate containing 0.01% triethylamine, and the extracts were analyzed according to ref 22.

**Controlled Introduction of Nicotine and Ethenylpyridine.** Nicotine and EP were fed directly into the chamber from all-glass diffusers swept by a flow of nitrogen (at 300 mL/min). These consisted of an ampule fused to a capillary tube (4 cm  $\times$  2 mm i.d.), the feed rate being adjusted by controlling their temperature ( $\pm 0.15^\circ\text{C}$ ). The devices were allowed to equilibrate overnight before any measurement was made or any experiment initiated. The feed rates of nicotine and EP were critical parameters in the interpretation of the results, and their accuracy was ascertained by different methods. The weight loss of the diffuser was first determined directly. Although accurate, this primary assessment was not sufficiently precise. The emitted amounts were thus directly sampled by fitting to the diffuser outlet a series of annular denuders coated with citric acid. The water washings were made basic, extracted, and quantified as above (22). Last,

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TABLE 1. Experimental Conditions, Steady-State Air Concentration ( $C_{st}$ ), and Quantification of Sinks Loading (Uptake of Slow Sink, Mass at Equilibrium, and  $k_e$  of Fast Sink) for Nicotine

experimental conditions					slow sink both calc:	fast sink direct estimation		fast sink nonlinear fitting	
sink material	RH (%)	ACH ( $h^{-1}$ )	feed rate ( $\mu g/h$ )	$C_{st}$ ( $\mu g/m^3$ )	uptake at steady state ( $\mu g/m^2h$ )	mass at equilib ( $\mu g$ )	$k_e$ (m)	mass at equilib ( $\mu g$ )	$k_e$ (m)
glass	41	1.0	136	98	6.2	198	0.34	150	0.26
glass	60	0.98	150	86	11.8	141	0.28	149	0.29
glass	72	1.0	148	69	13.2	200	0.48	161	0.39
glass	53	0.95	156	120	7.0	388	0.54	407	0.56
glass	60	0.49	155	195	10.1	399	0.34	343	0.29
glass	60	1.44	71	23	6.3	28	0.22	39	0.28
glass	69	0.73	182	123	15.4	n.d.	n.d.	309	0.42
cotton	38	1.0	142	26	51	646	12.2	673	12.8
cotton	72	1.11	131	24	33	287	5.8	223	4.5
cotton <sup>a</sup>	40	0.84	684	212	240	6440	15.0	8400	19.6
cotton <sup>a</sup>	32	0.72	1192	330	466	12500	18.8	15100	22.8
cotton	69	0.70	285	82	96	2180	13.1	1600	9.5
cotton	64	1.0	167	27	54	1235	22.7	n.d.	n.d.
cotton	53	1.0	148	25	52	930	18.4	n.d.	n.d.
cotton	50	0.55	138	28	51	n.d.	n.d.	n.d.	n.d.
nylon	76	1.13	130	40	16	429	5.2	440	5.3
nylon	41	1.0	137	80	18	287	1.6	210	1.1
nylon	62	0.98	147	132	19	700	4.8	n.d.	n.d.
nylon	62	0.49	148	71	19	n.d.	n.d.	n.d.	n.d.

<sup>a</sup> Steady state was not quite achieved, resulting in an underestimation of the fast sink capacity and discrepant values being obtained from adsorption versus desorption data sets.

the mass balance performed by chemical analysis of sink samples (see below) provided an a posteriori validation of the accuracy of the diffuser calibration.

**Sink Samples.** Two materials, commonly encountered in indoor covering and furnishing or in clothing and with different surface characteristics, were selected: cotton, which is rather hydrophilic, as indicated by its water regain, and nylon which is much less so (23). Both fabrics, purchased on the open market in Switzerland, appeared white, indicating minimal or no dyeing. More information about their origin or preparation was not acquired, since this study was aimed at outlining the differences among the fibers with respect to their affinity toward EP and nicotine, rather than performing a systematic study to obtain truly representative results for each class of fibers. For each test, two 1-m<sup>2</sup> samples of the material were machine-washed and fixed onto two faces of the chamber (loading factor of 2 m<sup>-1</sup>).

**Experimental Protocols.** Experiments started with an adsorption phase during which the compounds were fed into the chamber at a constant rate for 30–48 h, after which time a steady-state concentration could be observed. The system was then purged with clean air for up to 3 days (desorption phase). The modeling of the sorption processes was performed using the profiles of air concentrations in the chamber and the amounts found on small sink pieces (fabric or glass) deposited in the chamber.

Series of experiments were performed for each sink material with different air-exchange rates (from 0.5 to 1.6 ACH) and RH levels (from 30 to 70%) and selecting nicotine feed-rate so that its concentration at the end of the adsorption phase would stabilize between 23 and 330  $\mu g/m^3$ . The EP feed rate was not targeted to match the ratio to nicotine level commonly observed in ETS. Rather, levels ranging between 116 and 375  $\mu g/m^3$  were achieved to improve results precision.

The set of experimental conditions used throughout the study is found in Tables 1 and 2.

**Modeling and Data Treatment.** Figure 1 shows a nicotine concentration profile, including both adsorption and desorption phases, obtained with 2 m<sup>2</sup> of cotton in the chamber. The exponential curves that would be observed in the absence of sorption and assuming a perfect mixing (simple dilution model (24)) are also plotted.

**Modeling.** Within the time frame of the studies, two processes with distinct time scales could be recognized in the data profiles, as detailed below. The sorption dynamics could thus be adequately reflected by a two-sink scheme (three-compartment model), following refs 25 and 26.

First, the steady-state concentration at the end of the adsorption phase was often lower than expected (especially for nicotine). Verifying the accuracy of the feed rates (see Experimental Section, and mass balance below) ruled out an error in the diffuser calibrations. This implies a removal process with a constant rate throughout the later part of the adsorption phase. For low air levels and time frames of days as in this study, this can be treated as an irreversible removal. Choosing a first-order approximation simplifies the equations (it only adds to the chamber ACH).

Second, even after taking into account this first sink, the measured data are still lower than a simple dilution model prediction in the early part of the adsorption phase and higher at the onset of the desorption phase (Figure 1). This could be accounted for by adding a fast reversible sink to the scheme (loaded until saturation and then emptying in the desorption phase). The occurrence of a fast reversible sink in nicotine sorption was also noted in ref 18, although not addressed in the study.

The proposed scheme is represented in Figure 2, which also gives the equations and the notations. This model, introduced by Colombo et al. (25), has the advantage of being formally the same as Tichenor's "Two-Box" model (27) for which a mathematical treatment was developed (28). By using these equations, estimates for the rate constants ( $k_3$ ,  $k_4$ , and  $k_5$ ) could be obtained by nonlinear fitting.

**Computing Procedures.** The curve fittings were done using the SAS NLIN nonlinear regression routines. The performance of three optimization methods, namely DUD, Gauss, and Gauss–Newton, was compared. More convergence problems were experienced with the Gauss–Newton method than with the Gauss or DUD methods, the latter being in our case the best. The DUD algorithm is also simpler to use, since the explicit expressions of the first and second derivatives of the response function are not needed. This algorithm was thus used throughout the study.

TABLE 2. Experimental Conditions, Steady-State Air Concentration ( $C_{st}$ ), and Quantification of Sinks Loading (Slow Sink Uptake, Mass at Equilibrium, and  $k_e$  of Fast Sink) for Ethenylpyridine

experimental conditions					slow sink both calc:	fast sink direct estimation		fast sink nonlinear fitting	
sink material	RH (%)	ACH ( $h^{-1}$ )	feed rate ( $\mu g/h$ )	$C_{st}$ ( $\mu g/m^3$ )	uptake at steady state ( $\mu g/m^2 h$ )	mass at equilib ( $\mu g$ )	$k_e$ (m)	mass at equilib ( $\mu g$ )	$k_e$ (m)
glass	41	1.0	156	153	0.51	16	0.02	<1	<0.01
glass	60	0.98	0	0	—	—	—	—	—
glass	72	1.0	155	153	0.26	44	0.05	140	0.15
glass	53	0.95	130	136	<0.2	76	0.09	115	0.14
glass	60	0.49	190	357	2.4	125	0.06	218	0.10
glass	60	1.44	0	0	—	—	—	—	—
glass	69	0.73	190	157	n.d.	85	0.09	118	0.12
cotton	38	1.0	125	116	4.1	154	0.46	207	0.69
cotton	72	1.11	141	126	<1	214	0.65	209	0.63
cotton	40	0.84	142	160	3.2	357	0.92	348	0.89
cotton	32	0.72	212	280	~1	704	1.06	716	1.08
cotton	69	0.70	135	185	~1	150	0.21	195	0.33
cotton	64	1.0	0	0	—	—	—	—	—
cotton	53	1.0	0	0	—	—	—	—	—
cotton	50	0.55	134	220	—	449	0.82	n.d.	n.d.
nylon	76	1.13	159	141	~1	104	0.17	82	0.1
nylon	41	1.0	164	160	<0.5	33	?	25	?
nylon	62	0.98	0	0	—	—	—	—	—
nylon	62	0.49	0	0	—	—	—	—	—

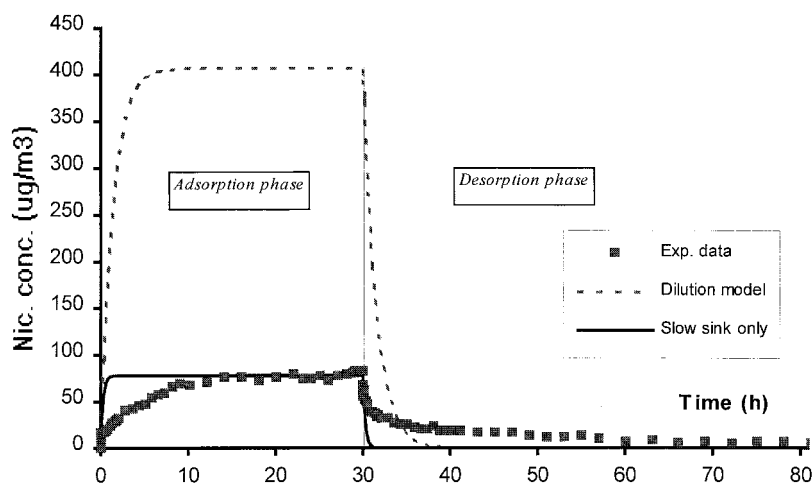


FIGURE 1. Nicotine concentration profile in an experiment on cotton material. The curves expected in the absence of any sink (dilution model) and when including only the slow sink as an irreversible removal have been added to the plot.

A useful feature of the chosen kinetic model is that the main parameters describing the process can be directly estimated without performing any curve fitting. With regard to the irreversible removal, comparing the removal rate  $K = k_1/(VC_{st})$  observed when air concentration is steady (at  $C_{st}$ ) to the (known) air-exchange rate  $k_2$  yields by difference the rate  $k_5$ . With regard to the fast sink, it has been shown (27) that the mass taken up by a reversible sink when fully loaded could be graphically calculated from the concentration curves. It is proportional to the area between the experimental concentration curve and the exponential that would be expected in the absence of the reversible sink. This area can easily be computed from the data using a trapezoid construction (19). Being based on a mass balance, the calculation yields a true estimate of the mass in the sink at equilibrium without any assumption on the kinetics of the underlying phenomenon. This treatment, referred to as the "direct estimation", was conducted on both sorption phases.

**Mass Balance for Confirmation of the Feed Rates.** The amounts sorbed onto the sink materials were determined by successive analysis of small pieces of glass, nylon, or cotton deposited in the chamber before starting the experiments.

A plot of the nicotine amounts recovered in cotton is given in Figure 3 (same experiment as Figure 1).

The amount  $W_{tot}$  of nicotine in the sink can also be calculated from the concentration curves in the adsorption phase independently of any assumption using the mass balance equation

$$W_{tot(t)} = k_1 t - k_2 V \int_0^t C(\theta) d\theta - VC_{(t)} \quad (1)$$

A graphical evaluation of the value of the integral is easily obtained for each data point  $C_{(t)}$ .

## Results

**Calculations of the Sorption Parameters.** *Slow sink.* Consistent values were found for the rate constant of the slow sink (irreversible removal),  $k_5$ , by direct estimation or by nonlinear fitting, and either from adsorption or desorption phase data.

To assess the sorption to fabric material, the contribution of the exposed chamber walls must be subtracted. A model for  $k_5$  as a function of RH and  $C_{st}$  was thus obtained for

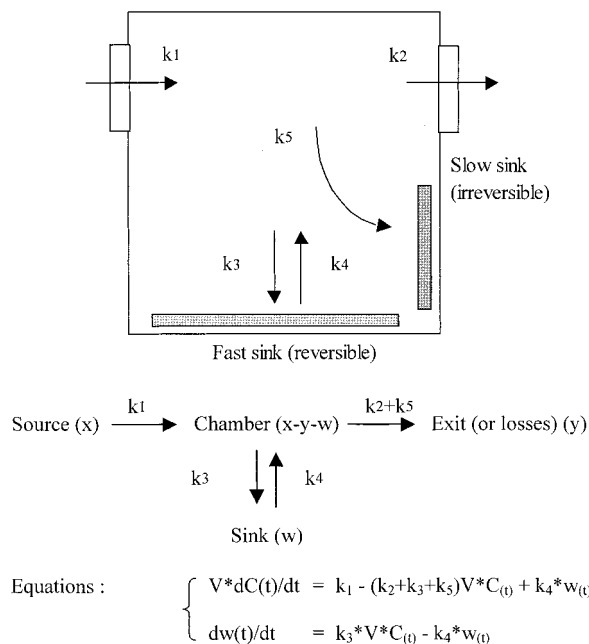


FIGURE 2. Kinetic scheme chosen as the model for EP and nicotine sorption.

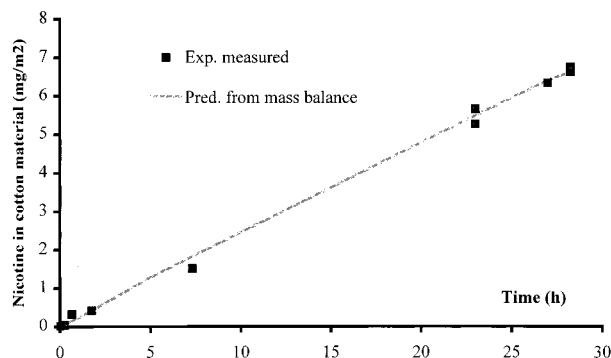


FIGURE 3. Profile of the mass found analytically in the sink compared to prediction from a mass balance (see text). Same experiment as in Figure 1.

nicotine sorption to glass, while the effect observed for EP was too small to be meaningfully evaluated in this way. Because of the relatively small amount of data, equally satisfactory fits could be obtained with several models. In particular, good results ( $R^2 = 0.943$ ) were obtained with an equation where RH (%) appears as an exponential, as proposed in ref 29, and where the nonlinearity of nicotine sorption as a function of air concentration is reflected by a power function as suggested in ref 18:

$$k_5 \approx AC_{st}^{\alpha} \exp^{\beta[RH]} \quad (2)$$

The empirical values of the parameters  $A$ ,  $\alpha$ , and  $\beta$  for nicotine sorption to glass are given in Table 3.

After correction, the mass uptake into the slow sink at steady state  $I_e = k_5 C_{st} V$  was computed for each material, and reported (per  $m^2$ ) in Tables 1 and 2. Finally, the corrected  $k_5$  values for the fabrics could also be fitted by eq 2, the best sets of parameters being reported in Table 3.

**Fast Reversible Sink.** There was considerable uncertainty on the determination of the  $k_3$  and  $k_4$  rates, but their ratio could be more precisely determined than the individual values (26). Under the assumption of a linear Langmuir isotherm, quite acceptable for nonfleece surfaces (27),  $k_3/k_4$

TABLE 3. Modeling the Values of the  $k_5$  Removal Rate for the Slow Sink<sup>a</sup>

	glass (empty chamber)	cotton (wall effects corrected)	nylon (wall effects corrected)
A	2.81	6.97	11.33
$\alpha$	-0.739	-0.238	-0.887
$\beta$	0.0310	-0.01028	-0.000295

<sup>a</sup> The equation:  $k_5 \approx AC_{st}^{\alpha} \exp^{\beta[RH]}$  (with  $k_5$  in  $h^{-1} m^{-2}$ ,  $C_{st}$  in  $\mu g/m^3$ , and RH in %) was used.

is proportional to the mass,  $M_e$ , in the sink at equilibrium divided by the air concentration (27, 28).

Curve fittings were performed on data from both adsorption and desorption phases and from their consolidation. The agreement between the amounts calculated as adsorbed and released from the fast sink was good in most experiments. For the sake of brevity, only an averaged result was reported. Values for the mass,  $M_e$ , were also obtained by the direct evaluation procedure. The intrinsic parameter representing the sink properties of a material is the equilibrium constant of its Langmuir isotherm  $k_e$ . It can be derived from the kinetic parameters when the sink effect is predominantly due to a material with a known surface,  $S$ , by  $k_e = (M_e/S)/C_{st}$  or  $k_e = (k_3/k_4)/S$ .

From the empty chamber results,  $k_e$  (glass) was calculated as  $(k_3/k_4)/6$ . When some walls were covered with fabric, an estimate of its  $k_e$  could still be obtained when  $k_3/k_4$  was substantially larger than  $4k_e$  (glass) (i.e., negligible effect of glass surfaces). Then  $(k_3/k_4)/2$  was reported as  $k_e$ . This was always realized for nicotine, but for EP only the mass adsorbed by the system as a whole could be reported in the nylon experiments. All results are found in Tables 1 and 2.

**Kinetic Scheme with a Two-Compartment Reversible Sink.** It was questioned whether the slow sink of the present model could be a deeper or more strongly bound state for molecules that would first have been reversibly adsorbed into a superficial sink. In this alternate scheme, the two sinks would be linked in series. Such a two-compartment sink model was shown, for instance, to provide a better prediction of the experimental data for the sorption of ethylbenzene to carpets when long-term, low-level emissions were of concern (30).

To test this hypothesis, a second kinetic model was constructed by adding to the model a transfer to and from a second sink. An irreversible removal was still maintained in this model to determine its contribution, if any. The corresponding set of differential equations was resolved mathematically and the equations for the solution fitted to the experimental data. Forcing the irreversible rate constant,  $k_5$ , to zero with the two reversible compartments in serial arrangement made it impossible for the model to fit the data. The best-fit results for  $k_5$  that were obtained using the model featuring this two-compartment reversible sink were not significantly different from those derived from the first model. Moreover, using the more complex model did not result in a statistically significant improvement of the fit, but, rather, led to over-fitting. It was concluded that a slow sink in parallel with the reversible sink remained a necessary feature. Without it, a second sink in series with the fast, reversible sink could not fit the data, even with a very slow desorption rate, making the second sink an irreversible one. A mechanism whereby the slow sink would be a larger and deeper stage, accessed from a previous fast and reversible stage, thus appeared incompatible with the data.

**Influence of Experimental Parameters: Averaged Result Table.** To highlight the respective influences of RH and of the sink material, the rates of EP and nicotine removal at two



**TABLE 4. Estimates of Uptake Rate into the Slow Sink and of Equilibrium Constant  $k_e$  to the Fast Sink at Relative Humidity of 40 and 70% (See Text)<sup>a</sup>**

material	uptake rate ( $\text{h}^{-1}$ )		$k_e$ (m)	
	at 40% RH	at 70% RH	at 40% RH	at 70% RH
Nicotine Concentration $100 \mu\text{g}/\text{m}^3$				
glass	0.05	0.14	0.3	0.4
cotton	1.54	1.16	18–22	4–9
nylon	0.19	0.19	2	5
Ethenylpyridine Concentration $150 \mu\text{g}/\text{m}^3$				
glass	0.003	<0.002	n.d.	$\approx 0.15$
cotton	0.03	0.01	1.1	0.7
nylon	0.02	<0.001	<glass	<glass

<sup>a</sup> For the fast sink the rates were directly calculated from experimental results obtained at the appropriate RH (linear Langmuir isotherm). For the slow sink, eq 1 was used for predicting nicotine rates. In the case of EP, sizable numbers could only be obtained for sorption to cotton material, and the reported numbers are the averages of the results from experiments in which relative humidity was 38 and 40%, and 72 and 69%, respectively. On average, the steady-state concentrations were  $150 \mu\text{g}/\text{m}^3$  in these four experiments and they were within a  $35 \mu\text{g}/\text{m}^3$  range from this value.

different RH levels were estimated for each material (see Table 4).

## Discussion

**A. Dual-Sink System.** The proposed model calls for two concurrent sorption processes differing widely in their time scales. The first one appeared as an irreversible process as it was so far from saturation at the end of the adsorption phase (up to 3 days in this study). The second was saturated within hours so that its more limited capacity could readily be estimated.

Many sorption studies only recognize one sink, a reversible one, because it is by far the dominant phenomenon for compounds with a higher volatility. The occurrence of a second slower sink was, however, manifest in several studies (11, 14, 26). From results obtained on homologous alkanes (31) it was clear that the impact of the slow sink increased with the compounds' boiling point. It is, for nicotine, a vastly prominent feature. In fact, the recent work on nicotine sorption (18) essentially focused on this sink, as the authors first saturated the whole system with large nicotine levels.

That sorption was stronger for pollutants with lower vapor pressures was apparent from many studies reporting total sorbed amounts (32). These amounts were found to be inversely proportional to the logarithm of the vapor pressure in a study using a system with two completely reversible sinks (15), consistent with linear adsorption isotherms rather than absorption phenomena.

In this study, chemical analysis of sink materials clearly confirmed that in both sink processes the compounds were not degraded nor covalently bound. This is consistent with other observations that even compounds collected in the slower sink could be released unchanged, albeit at a very slow rate (33, 34). Re-extraction of nicotine from steel surfaces was reported to be incomplete, however, when all sinks were completely saturated at the onset of the experiment (18).

**B. Impact of the Experimental Conditions on the Kinetic Parameters.** The impact of temperature on sorption processes has previously been shown to be relatively moderate (23, 34). The uptake of 2-butoxyethanol was only doubled by a  $14^\circ\text{C}$  increase (14). Such changes in indoor temperature are not expected, and the study's design was thus restricted, for each sink, to the effects of varying RH and the compounds' concentrations in the chamber air.

**1. Influence of Relative Humidity [RH] and Sink Material.** Due to its high concentration in air, water will tend to form

a film on a solid surface (35). The description of sorption phenomena will thus result from the combination of two contributions.

First, the sink surface area will be modified (blocking of active sites or filling of pores by water; and swelling or fibril relaxation in cellulose fibers). Second, as the compound's water solubility is increased, its interaction with the surface of the water film or its dissolution in it will also increasingly contribute to the process (35, 36). Thus, the interaction of a VOC with the outer layers of the water film may be a determining step (14, 36), and vapor pressure alone is not sufficient to determine a compound's propensity to sorption. For instance, an inverse exponential relationship was found between the mass of VOC adsorbed onto quartz and RH, but highly water soluble compounds such as methanol deviated from this (29). Decane sorption to cotton decreased rapidly with an increase in water coverage as moisture uptake competed for the fiber surface (37). A recent study assessed quantitatively the contribution of the water solubility factor of a VOC to the strength of its sorption to carpets, wall covering, and gypsum board (15).

Nicotine is very water soluble and will partition about equally between water and hexane (38). The water solubility of EP is much lower ( $2.75 \text{ g}/100 \text{ g}$  at  $20^\circ\text{C}$  for the 4-isomer (39)).

Summarizing the influence of RH on nicotine and EP sorption, Table 4 shows two major points.

First, the influence of RH on the sorption processes is quite significant. A change from 40 to 70% resulted in the sorption parameters varying by a factor of typically 2 to 3.

Second, changing RH has a quite different influence depending on the material surface. On glass, the rate of nicotine uptake into the slow sink increased substantially (by a factor of 2.5) when RH was increased, and  $k_e$  for the fast reversible sink increased slightly. This suggests that dissolution in the water film is sufficient to more than offset the loss of interaction with the glass active sites. In the case of EP, the precision of both determinations was insufficient to estimate a trend. The cotton experiments showed a substantial decrease of both nicotine and EP sorption when RH was increased, and more so for EP than for nicotine. Thus, in line with the results on decane sorption (37), dissolution in the water film could not compensate in this case for the reduction in surface area and pore volume, especially for the less water soluble EP. Finally, RH effects for nylon appear intermediate between those observed on glass and on cotton.

**2. Effect of Gas-Phase Concentration.** At the end of the adsorption phase, the rate of slow-sink sorption was found to be a nonlinear function of the steady-state concentration. For nicotine, after correcting for RH effect, an inverse relationship was found between  $k_s$  and a fractional power of  $C_{st}$  (Table 3). For EP the results did not permit a quantitative evaluation, but qualitatively exhibited the same trend.

These results are consistent with the measured nicotine uptake by human hair (17). Treating these data in a way consistent with the present study showed sorbed amounts to be proportional to  $C_{st}^{0.75}$  (levels of 20 to  $2000 \mu\text{g}/\text{m}^3$  for 3 days). The slow sink is largely preponderant in such an experiment, so that this yields a value of  $-0.25$  for  $\alpha$  (using eq 2), comparable to that found for cotton (Table 3). The latest nicotine study (18), also overwhelmingly depicting the slow-sink loading, exhibited the same nonlinear trend. Treated as in the present study with the same units, these data would point toward a value of  $-0.54$  for  $\alpha$ . This latter case is rather different, however, in that the sink loading was pushed to its saturation.

Altogether, it would appear that the slow sink is well-described by a Freundlich isotherm.

Some nonlinearity in the fast sink loading with respect to  $C_{st}$  (i.e., a deviation from a Langmuir behavior) could not be ruled out, but it was much smaller than in the case of the slow-sink removal, and its precise quantification would not be feasible.

**D. Impact of Sorption on the Validity of Using Nicotine as an ETS Marker.** It is well-recognized that sorption processes will make nicotine disappear faster from fresh ETS as compared to other gas-phase components (5, 40). Most of the time, the fact that sorption effects quickly reduce its level is implicitly taken into account when using nicotine as a marker. This is because when an assessment is associated with a nicotine level, the ratio to be used is often derived from a set of reference situations during which adsorption has also taken place. The re-emission of this adsorbed nicotine, however, could be the cause for biases that are generally overlooked but could be important in certain situations.

A first kind of bias is when an assessment is made some time after a smoking event, when the room ventilation has removed most of the smoke. Nicotine re-emission from the room sinks may add a disproportionate amount to that derived from ETS residual levels. See for instance refs 41 and 42 and the examples reviewed in ref 5. Biases may be expected when ETS exposure is assessed by discrete samplings where sparse, intermittent smoking is taking place. In addition, taking into account sink effects has been shown through numerical simulations (9) to be very important when relating emission rates and air concentrations. Neglecting sinks can lead to errors of up to 25–100% when the air-exchange rate is significantly lowered during the night or the weekend. Concern about biases was also expressed by Ogden (43), when a continuous sampling is performed over several days with passive samplers in a building where smoking takes place during working hours as was done in ref 44. In their reply (45), these authors estimated at about 20% the relative error that resulted from the desorption of nicotine.

The importance of these effects can be quantified using the results of the present study if EP is taken as representative of an ETS gas-phase component. The measured EP concentration can be compared to what would be calculated by using nicotine as a marker, i.e., nicotine concentration multiplied by the ratio of the compounds introduction rates. In experiments with cotton as a sink material, overestimations by a factor of 2 to 3 are seen after a day of sink desorption.

Another kind of bias happens when a disproportionate amount of nicotine is adsorbed from ETS onto a mobile surface such as dust (46) or a person's clothing and later released. Providing estimates of the amounts of nicotine and EP that can be sorbed and released within a short time in sinks, the present study may help quantify this effect. The fast sorption process will adsorb on 1 m<sup>2</sup> of cotton cloth 0.8 to 1.1 mg of nicotine when its gas-phase concentration is 82  $\mu\text{g}/\text{m}^3$ . In an ETS situation, where a nicotine/EP ratio of 5 is often found (5, 6), the corresponding EP level would be about 16  $\mu\text{g}/\text{m}^3$ . Using the present results, about 13  $\mu\text{g}$  (i.e., about 1% of the nicotine amount) of EP would be loaded in the fast sink in this case. The re-emission of micrograms of EP over hours would have a negligible impact on air concentrations, but the mass of nicotine released in this example would be about one-fourth of the sidestream smoke yield of one cigarette (1).

Field studies that could demonstrate an overestimation of ETS levels due to nicotine transport and re-emission are those where a tracer gas ( $\text{SF}_6$ ) was released, together with ETS, to check for smoke leakage. Examination of such results (47) shows indeed that when transport by diffusion or recirculation is minimal (very low  $\text{SF}_6$  recoveries) the estimations of "ETS leakage" based on nicotine are often higher than the true value (from  $\text{SF}_6$ ). Both estimations correlate

much better, though, when direct transport of ETS can be suspected (higher  $\text{SF}_6$  recoveries), and the estimate from nicotine is then the lowest. Sink effects may also explain why traces of nicotine (or its metabolites) were found in the body fluids of individuals that had not been exposed to ETS, as was for instance reported in the study of Pirkle et al. (48).

Finally, it should be mentioned that the above numbers are a conservative estimate. A desorption performed into clean air, resulting in faster exchange kinetics, might also show a contribution from the slow sink desorption which could not be observed in this study.

## Acknowledgments

The authors would like to thank Dr. M. Graf-Jaccottet, Dr. U. Graf, and Mr. M. H. Jaunin, of the Neuchâtel University, for their contribution in the mathematical modeling and the data fitting, Ms. L. Posset, Ms. A. Zwahlen, and Mr. Y. Genoud for their contributions in the experimental work, and Drs. J. Zuber and D. Braem for their helpful discussions.

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Received for review June 23, 1998. Revised manuscript received January 4, 1999. Accepted February 1, 1999.

ES980640Q