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Thirdhand Smoke at Philip Morris

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ABSTRACT

Introduction: Thirdhand cigarette smoke is the fraction of cigarette smoke that remains in the environment long after a cigarette is extinguished.

Methods: The Truth Tobacco Documents collection at UCSF was searched for information on thirdhand smoke.

Results: In 1991, scientists at Philip Morris Inc. conducted some of the first studies on thirdhand cigarette smoke. For 110 days, 8 hours a day, they ran sidestream cigarette smoke through a 30 m^3 room that contained carpet, curtain and textured wallpaper. The room was ventilated with clean air every night. By comparing the chemicals in the air during the 8 hour smoking period and during the clean air ventilation period they showed that some smoke chemicals persist in the air 12 hours after smoking. By extracting the nicotine and nitrosamines from samples of the carpet, curtain and wallpaper, they found that high concentrations of nicotine and the carcinogen 4-(methylnitrosamino)-1-(3-pyridyl)-1-butanone (NNK) persisted in the room for over 50 days, that surface chemistry affected nitrosamine concentrations and that the concentration of NNK in the room, 110 days after the last cigarette was extinguished, could exceed the mass of NNK that entered the room as smoke.

Conclusions: These data, from a controlled environment where the total number of cigarettes smoked is known, provide further evidence that cigarette smoke chemicals remain in the environment for months after smoking, that they re-emit back into the air and that they react to form new toxins and carcinogens. Smokefree policies are the best method to reduce exposure to thirdhand smoke.

IMPLICATIONS

This unpublished, original research from Philip Morris Inc. demonstrates that majority of the nicotine and tobacco-specific nitrosamines in the secondhand smoke from each cigarette smoked indoors remains on indoor surfaces for months after the cigarette is extinguished. It also demonstrates that elevated concentrations of nicotine, ammonia, formaldehyde and the gas-phase nitrosamine, N-nitrosopyrrolidine, can be found in the air for over 12 hours after smoking, that surface chemistry affects nitrosamine formation and persistence and that the amount of the carcinogenic nitrosamine, 4-(methylnitrosamino)-1-(3-pyridyl)-1-butanone (NNK) that persists months after smoking ends can exceed the amount that actually came out of the cigarettes.

INTRODUCTION

Thirdhand cigarette smoke (THS) is a term for the chemicals in cigarette smoke that linger in the environment after a cigarette is extinguished. In a consensus paper published in 2011, public health scientists defined THS as residual tobacco smoke pollutants that:

1) Remain on surfaces or in dust after tobacco has been smoked
2) Re-emit into the gas phase, and/or
3) React with other compounds in the environment to produce secondary pollutants[1].

Recent research has shown that tobacco smoke contamination in real world indoor environments can reach high levels[2] and can persist for months[3, 4]. Exposure to THS can cause increases in biomarkers of tobacco smoke exposure in nonsmokers who are not exposed to secondhand smoke (SHS)[5, 6]. There is evidence that the aging of smoke causes increases in toxicity. [7]. Recent in vitro studies have shown that exposure to THS can damage DNA[8], impair cell proliferation[9, 10], motility[9] and metabolism[11] and cause increases in reactive oxygen species and oxidative stress.[12, 13] In vivo exposure studies have shown that THS exposure can damage multiple physiological systems.[14] Exposure of adult mice impairs wound healing[15] and causes lung inflammation[15], hyperactivity[15], liver steatosis, insulin resistance[16], metabolic syndrome[16] and increased clotting[17]. Prenatal and early postnatal exposure affects weight gain and alters white blood cell counts during adulthood.[18] These findings show that THS is toxic, persists in real indoor environments and may be harmful to human health.

The research to date does not include controlled, longitudinal studies that can give a clear idea of the fate of cigarette smoke chemicals in the complex conditions that prevail in most indoor environments. Here we present data from the Truth Tobacco Documents Library showing that, between 1989 and 1992, Philip Morris Inc. (PMI) conducted experiments over the course of 110 days on the fate, persistence and chemical reactions of THS in a controlled experimental chamber. This previously unpublished research includes novel findings that advance our understanding of the chemistry and kinetics of THS in realistic indoor environments.

METHODS

Tobacco Industry Document Searches

The preliminary data for this study were discovered during earlier investigations of research performed by PMI on how aging changes the chemistry and toxicity of sidestream cigarette smoke[7, 19, 20]. Between March, 2014 and June, 2017 we searched the University of California, San Francisco Truth Tobacco Industry Documents at (https://www.industrydocumentslibrary.ucsf.edu/tobacco/), using snowball strategies[21], starting with study numbers assigned to PMI experiments that we discovered during our preliminary investigations and other keywords, including “nitrosamine,” “nicotine,” “sidestream,” and

"RASS" (room-aged sidestream). We found 41 unique documents which were analyzed in conjunction with associated publications in the open scientific literature by PMI. These documents include experimental designs for the projects, informal logs of daily and weekly progress, laboratory notebooks, reports prepared for internal presentations, and project summaries.

Derivation, Graphing and Analysis of Data from Tobacco Documents

The data on chemical concentrations that are analyzed and presented in this study were all extracted from the tobacco documents as numerical data. We copied chemical concentration data from the tobacco documents into spreadsheets and plotted graphs and calculated summary statistics and T-tests using Excel (Microsoft, Inc. Redmond, WA). We did not abstract any data from graphs in the tobacco documents. Direct quotes from tobacco industry documents are presented within quotation marks and cited.

Philip Morris Aged Sidestream Smoke Generation

2R1 Kentucky Reference cigarettes were smoked using a 30-port smoking machine [22] [23] according to ISO 3308 [22]. The sidestream smoke was collected by a hood above the cigarettes and directed via a duct (epoxy coated, cross sectional area 0.2 m^2) into the 30 m^3 aging room. [22, 24] Mainstream smoke was discarded.

The materials in the smoke aging room were: 11 m^2 of carpet, pure wool on polymer base; 26 m^2 of curtain, pure wool; 29 m^2 of wallpaper, rough structured and painted with latex paint; and 2 m^2 of glass [23, 25]. The aging room was maintained at 23°C and 44.2 % relative humidity, on a daily light cycle [26]. The fresh smoke was diluted with filtered temperature- and humidity-controlled air to achieve a CO concentration of ~28 ppm, and then was passed through the smoke aging room at a rate of 266-291 l/min, resulting in an average smoke age of 1-1.1 hours at the outlet. [27, 28] Approximately 110 cigarettes were smoked per day.[29]

This resulted in a concentration of approximately 9 mg total particulate material (TPM) per m^3 at the inlet to the aging room and 2.5 mg TPM/m^3 at the outlet, measured gravimetrically.[25] Smoke was run through the aging room 8 hours a day for a total of 105 days.[26, 30] After each 8 hours of smoke generation, the aging room was flushed with clean, filtered air for 16 hours at 0.58 air changes per hour (ACH). After smoke generation stopped, the room was ventilated continuously at 0.62 ACH.[27, 31]

Philip Morris Air Sample Collection and Analysis

The methods for TPM, CO, CO2, nicotine and aldehydes are in Hausmann et al.[27]. The nitrosamine samples were collected at 2 l/min for 2 hours on conditioned Extrelut sampling media.[32] The analytical methods are not described in detail, but it is likely that they were similar to those used in earlier studies of air-borne nitrosamines performed in Cologne[19].

Philip Morris Surface Sample Collection

Two samples of each surface material (curtain, carpet, wallpaper, glass) were collected per time point from random sites in marked grids[33]. 5 cm x 5 cm pieces were cut from the carpet and curtain, 10 cm x 10 cm from the wallpaper. Glass samples were collected by wiping areas of 20 cm x 20 cm and 20 cm x 5 cm, respectively, using tissue paper soaked with citrate buffer and butylacetate solutions, respectively. Additional samples were collected from the carpet as follows: a weighted box, wrapped in fiberglass filter paper was dragged across a 0.2 m^2 section of the carpet.[33]

Philip Morris Extraction and Analysis of N-Nitrosamines from Solid Substrates

Samples and unexposed control samples of the same materials were analyzed within 4 days of collection.[33] Initially, N-nitrosamine samples were transported in 100 ml citrate buffer. On day 30 of the experiment, they changed to transporting the nitrosamine samples dry and eluting in citrate buffer at the analytical laboratory.[31] The citrate elution buffer was washed with 100 ml of dichloromethane (CH_2Cl_2) and extracted in 100 ml CH_2Cl_2 3X. The organic phase was washed with 20 ml of 2N NaOH, dried over Na_2SO_4 and evaporated to 2 ml volume. 200 µl of internal standard calibration was added, and the sample was filtered and evaporated to 200 µl with N_2. 2 µl was used in GC [34].

RESULTS

Overview of Studies

In 1991, researchers at PMI began Project 3169, a 90-day inhalation study with the following objectives: to "compare the biological activity of "**conditioned" sidestream smoke (CSS**) obtained by **aging** and **contact with surface materials** found in **homes**, and **fresh sidestream smoke**[35]" (FSS) and "determine the chemical and physical parameters of the FSS and CSS as a basis for correlations with the biological activity." (Emphases from the original.) "Conditioned" sidestream smoke was generated by passing fresh smoke through a 30 m^3 room, about the size of an office or small living room. Transit through this room allowed the smoke to come into contact with common household materials before it was piped to rats for inhalation [35]. The goal was to replicate the environment of a smoker's home.

The preliminary documents describing project 3169 date from August and September, 1990[36, 37] and the last animal dissections were performed 9/12/1991[38]. In preparation for Project 3169, PMI researchers set up three systems to create aged sidestream cigarette smoke: one in Germany and two in Belgium[30, 36]. Each system had three separate, adjacent rooms for the smoking machine, smoke aging room and animal exposure chambers (Supplementary Figure 1).[26, 39] Preliminary chemical analyses on the effects of indoor surface materials on smoke chemistry were conducted in Germany and Belgium[36]. The animal studies and the later chemical studies were conducted in Belgium.

There were at least two subprojects associated with project 3169 which were designed specifically to analyze THS: the 24-hour profile of smoke chemistry (Project 5223) and deposition and persistence of nicotine and nitrosamines in the aging room (Project 5228). These projects appear to have been initiated in response to the findings of the routine chemical analyses of smoke done in Project 3169. The first mentions of these projects appear in June (5223) and July (5228) of 1991, toward the end of project 3169[38]. The design and approval for the THS projects appears to have been rapid and somewhat provisional. The experimental plan for project 5223 was drafted 7/25/91[32], 10 days after some of the first samples collected had been collected[40, 41]. It states, "The parameters listed in the tables will not necessarily be determined all". Limited resources at CRC or INBIFO may reduce the number of parameters and samples analyzed."[32] "CRC" refers to the Contract Research Center in Belgium, INBIFO is the "Institüt fur Biologische Forschung", in Germany. The experimental plan for project 5228 was written one day before the first samples were collected[38, 42].

Preliminary Smoke Chemistry Experiments for Project 3169

Prior to the start of the animal exposures, PM scientists tested the effects of 20 different combinations of wall surfaces and furnishings on the concentrations of TPM, nicotine, formaldehyde, acetaldehyde, acrolein, ammonia, and hydrogen cyanide [43]. The effects were measured by comparing the concentration of a chemical in smoke before entry into and after exit from the aging room (See Supplementary Figure 1). The control condition was epoxy-coated wallboard on the walls and ceiling, and vinyl flooring. After control tests, they tested the addition of rough-textured wallpaper, painted with latex interior paint, carpet, a bookcase with books, different kinds of curtains and other materials.

90 minutes of aging under control conditions caused the following changes: TPM decreased by 34%, nicotine by 69%, hydrogen cyanide by 17% and acrolein by 27%. Formaldehyde and acetaldehyde remained unchanged. The combination of textured wallpaper that had been painted with latex paint, a wool curtain, wool carpeting, and a wooden bookshelf, achieved maximum changes in the smoke chemistry: 64% less TPM, 91% less nicotine, 94% less ammonia, 78% less formaldehyde, 56% less hydrogen cyanide and 18% less acrolein than in fresh smoke.[44] Painted wallpaper, wool curtain and wool carpet were used in Project 3169[45].

Routine Smoke Analyses, Project 3169

There was some variation in smoke concentration and air flow during the first 14 days of the exposure. However after day 15, TPM and nicotine deposition percentages were consistent throughout the 90-day animal exposure study, evidence that the surface materials in the aging chamber did not saturate over time.[28] During Project 3169, the average decrease in TPM from fresh to aged smoke was 71%. [27, 43] The average decrease in nicotine was 76.5%. The average decreases in formaldehyde, ammonia and hydrogen cyanide were 70%, 62% and 53% respectively. There were slight increases (2.5%) in the concentrations of nitrogen monoxide and mixed nitrogen oxides and no changes in the concentrations of acrolein, 1,3-butadiene, benzene, toluene and isoprene.[28] The concentration of heavy metals in the TPM was tested once during the study. The filters used to collect the heavy metal samples had high background levels of heavy metals and only cadmium could be quantified. Aging decreased the aerosol concentration of cadmium by approximately 40%[26].

24-Hour Profile of Smoke Chemistry (Project 5223):

For Project 5223, the concentration of chemicals in the air of the aging room were measured during the 8 hour smoke generation period and during the 16 hour ventilation period. The target chemicals in the experimental plan included TPM, CO, CO_2, nicotine, aldehydes, ammonia, hydrogen cyanide (HCN), benzene, toluol, isoprene, 1,3-butadiene, hydrocarbons, polycylic aromatic hydrocarbons, tobacco-specific nitrosamines, volatile nitrosamines, mixed nitrogen oxides and nitric oxide. The goal of Project 5223 was to measure deposition and re-emission of the chemicals by comparing their concentrations in the air, during smoking (in fresh and aged smoke) and during the ventilation period.[32]

24 Hour Profile Results

As shown in Table 1, the airborne concentrations of ammonia, formaldehyde, N-nitrosopyrrolidine (NPY), nicotine and NNK decreased with aging. After 12 hours of ventilation, acetaldehyde and NNK were close to background levels and ammonia, formaldehyde, NPY and nicotine were still found in the air in the aging chamber. The N-nitrosodimethylamine (NDMA) data were too inconsistent to draw conclusions from. None of the chemicals were detected in the conditioned, filtered air used for diluting the smoke and ventilating the aging room. [27, 40, 41, 46]

The hydrocarbon and polycylic aromatic hydrocarbon analyses were not carried out. [26] The filters used to collect the heavy metal samples had high background levels of heavy metals and only cadmium could be measured. This is because metals analysis requires the use of special filters and vessels that are free of traces of the target metals[47]. Aging decreased the aerosol concentration of cadmium by approximately 40%, but there were no data for after ventilation.[26] We did not find data for TPM, CO, CO2, benzene, toluol, isoprene, 1-3, butadiene, or nitrogen oxides from this experiment.

Table 1: Concentrations of Airborne Chemicals in Aging Room

	Ammonia (µg/l)	Formaldehyde (PPM)	Acetaldehyde (PPM)	NPY (ng/l)	Nicotine (µg/l)	NNK (ng/l)
Clean air	n.d[27]	<0.02[27]	<0.04[27]	n.d.[25]	<0.05[27]	n.d. [25]
Fresh sidestream smoke	3.71[27]	0.54[27]	0.68[27]	0.13[25]	2.21[27]	0.61[25]
Aging room during smoke (% Fresh)	1.68 (45%)[48]	0.14 (26%)[49]	0.68 (100%)[49]	0.054 (42%)[40]	0.52 (24%)[41]	0.30 (49%)[40]
Aging room after 12 h vent (% Fresh)	0.96 (26%)[48]	0.07 (13%)[49]	0.02 (3%)[49]	0.045 (35%)[40]	0.31 (14%)[41]	n.d. (0%)[40]
Molecular wt (g)	17.01	30.03	44.05	100.12	162.23	207.23
Log K_{ow}*	0.23	0.35	-0.17	0.23	1.17	0.00[#]

n.d. = Not detected
*K_{ow} is the partition coefficient between octanol and water, estimated by EPA KOWWIN version 1.67. Lower numbers indicate hydrophilic compounds, higher numbers indicate hydrophobic compounds.
[#]NNK K_{ow} is zero because it is a solid at the temperature used in the model.

Deposition and Persistence of Nicotine and Nitrosamines in the Aging Room (Project 5228)

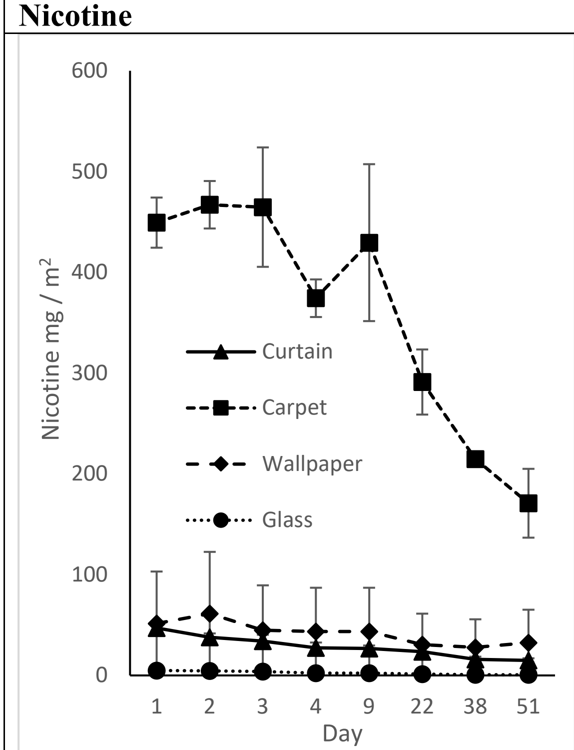
The experiments of Project 5228 were performed after smoke generation ended, when the aging room was continuously ventilated with clean air. The questions Project 5228 sought to answer were:

1. How much nicotine and nitrosamines do different materials absorb?
2. How long do nicotine and nitrosamines persist in these materials[33]?

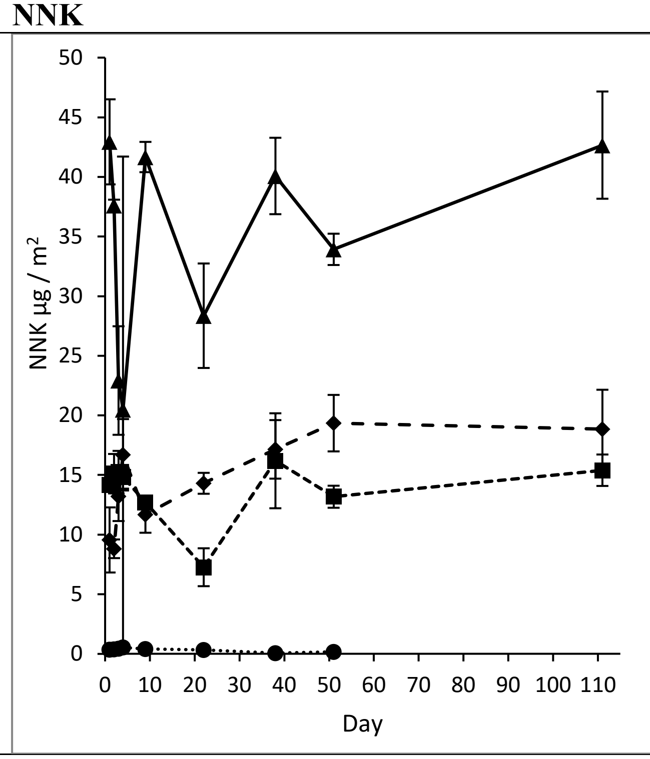
The experimental plan states that the project, "will be continued for several weeks or until no further traces of the analytes can be determined."[42] We found nicotine and nitrosamine data from the samples collected 1, 2, 3, 4, 9, 22, 38 and 51 days after the last day of smoke. We found nitrosamine data for the same time points as for nicotine, plus an extra set of samples for all substrates except glass, collected at 111 days. We also found data from an experiment, performed on day 2, where filter paper-wrapped weights were dragged across the carpet in the aging room and the filters tested for nicotine and nitrosamines. [26, 30, 34]

Figure 1: Persistence of Nicotine and NNK on Indoor Surfaces[34]

Nicotine



NNK



After 110 days of smoke exposure, the smoke aging room was ventilated continuously with clean air and small swatches of the surface materials were collected to test for the persistence of THS. The samples were extracted and the concentrations of nicotine and NNK were measured by gas chromatography and mass spectroscopy using known standards. Each data point represents the average of two swatches and each error bar represents the standard deviation. Only NNK was measured in the samples collected 111 days after the last smoke exposure. The curtain was 100% wool. The carpet was 100% wool on a backing made of other materials. The wallpaper was a textured type that had been painted over with latex interior wall paint. The chemicals sorbed to the glass were measured by wiping a defined area of the glass with a tissue and extracting chemicals from the tissue. Please see "Philip Morris Sample Collection" for further details.

Persistence of nicotine and nitrosamines

Nicotine and nitrosamines were detectable in all the materials in the aging room at 51 days. The concentration of nicotine in all of the materials decreased in a time-dependent manner (Figure 1).[34] The experiment was not powered to detect differences using repeated measures analysis. However, when the samples from the early (days 1-22) and late (days 38 & 51) periods of the experiment were pooled and compared, the differences were statistically different, with P values below 0.01, using the paired T-test. For example, the decrease between days one and two and days 38 and 51 was 64% for curtain, 58% for carpet, 46% for wallpaper and 85% for glass.

The concentrations of 4-(methylnitrosamino)-1-(3-pyridyl)-1-butanone (NNK) in curtain, carpet and wallpaper did not appear to decrease (Figure 1).[34] These analyses had higher standard deviations. There is some evidence of a trend toward increasing concentration of NNK on the wallpaper substrate, as the concentration at 111 days is 50% higher than the average concentration from days 1-9. The nitrosamines N-nitrosonornicotine (NNN), N′-nitrosoanatabine (NAT), NDMA, NPY and N-nitrosoanabasine (NAB) were also detected in the surface material samples, but at much lower concentrations (see supplementary materials).

Distribution of Nicotine and NNK in the Aging Room

The highest concentrations of nicotine were found in the carpet (450 mg/m^2), followed by wallpaper and curtain with approximately 9-fold less nicotine and glass with 92-fold less nicotine at day 1 (Table 2). The highest concentrations of NNK were found in the wool curtain (42.94 µg/m^3), followed by the carpet and wallpaper with approximately 3-fold less NNK and glass with 118-fold less NNK at day 1 (Table 2). Experiments described in the supplemental material showed that nicotine and nitrosamines could transfer from the carpet to other surfaces through friction.

Table 2. Nicotine and NNK Extracted from Indoor Materials [34]

Day	chemical	Curtain	Carpet	Wallpaper	Glass
1	Nicotine (mg/m^2)	47.10 ± 4.53	449.30 ± 24.89	51.55 ± 0.07	4.90 ± 1.13
	NNK (µg/m^2)	42.94 ± 3.57	14.18 ± 0.20	9.56 ± 2.73	0.36 ± 0.04
2	Nicotine (mg/m^2)	37.95 ± 3.75	467.05 ± 23.55	61.30 ± 8.77	4.40 ± 0.99
	NNK (µg/m^2)	37.60 ± 0.48	15.11 ± 1.65	8.81 ± 0.78	0.38 ± 0.05
38	Nicotine (mg/m^2)	15.85 ± 2.76	214.75 ± 7.28	27.85 ± 0.07	0.75 ± 0.07
	NNK (µg/m^2)	40.08 ± 3.20	16.19 ± 3.98	17.15 ± 2.45	0.07 ± 0.00
51	Nicotine (mg/m^2)	14.90 ± 2.12	170.85 ± 34.15	32.60 ± 4.67	0.60 ± 0.42
	NNK (µg/m^2)	33.92 ± 1.31	13.18 ± 0.92	19.35 ± 2.37	0.17 ± 0.14
111	NNK (µg/m^2)	42.66 ± 4.50	15.40 ± 1.32	18.86 ± 3.29	

Nitrosamine data are from pages 17-39 of document, Nicotine data are from page 151[34].

Aging Chamber: Total Nicotine and NNK Mass and mass balance

By multiplying the total surface area of each material by the mass per m^2, Philip Morris scientists calculated the amount of nicotine and NNK deposited in the chamber: 8 grams of nicotine and 15.3 milligrams of NNK.[29] A note at the bottom of the table, “as far as retrievable,” appears to acknowledge that extraction of these chemicals from the surface materials may not have been complete. There were approximately 11,000 cigarettes smoked during the entire smoke exposure.[29] A 2R1 research cigarette delivered 3.8 mg of nicotine to the sidestream, in tests performed by PM at the time of these experiments.[29] So, the nicotine in the room at the end of the 100 days of smoke exposure was equivalent to the total nicotine content of the sidestream of 2,049 cigarettes. After 51 days of constant ventilation, the nicotine was equivalent to 858 cigarettes. The 2R1 NNK yield was 1.1 μg/cigarette[29]. So, the nicotine in the room at the end of the 100 days of smoke exposure was equivalent to the total NNK content of the sidestream of 16,726 cigarettes. After 111 days of constant ventilation, the NNK was equivalent to 19,918 cigarettes. Using the air concentrations from project 5223 and the surface concentration data from project 5228, Philip Morris chemists calculated mass balances for nicotine and NNK in the smoke aging room at the end of the 100 days of smoke exposure (Table 3).[29] When they added up the masses lost to ventilation and the masses deposited in the aging chamber, they found that 60% of the nicotine that entered the room was recovered and 170% of the NNK that entered the room was recovered.

Table 3. Nicotine and NNK Mass Balance[29]

	Nicotine		NNK	
	g	%	Mg	%
Input	42	100	12	100
Exhaust	16	40	5	43
Surface deposition	8	20	15	130
Recovered	**24**	**60**	**20**	**170**

The End of Project 5228

The samples of carpet, wall paper and curtain for the last recorded nitrosamine analysis were collected December 8th, 1991[26]. On April 24th, 1992, a final set of samples were collected and the room was disassembled. The project information notes “There is still a very marked smell in this room” [30]. We found no evidence that the final set of samples were analyzed.

Publication of Findings by Philip Morris Inc.

The data on changes in aerosol smoke chemical composition over time were published in a short paper in 1994[23] and the chemical composition of fresh and aged smoke were published as part of the an inhalational toxicology paper in 1998[27]. However, the evidence showing persistence of nicotine and tobacco-specific nitrosamines for months on indoor surfaces, formation of NNK and the emission of nicotine and volatile nitrosamines from exposed surfaces, was not published.

DISCUSSION

These experiments were among the first to study the chemistry and persistence of thirdhand cigarette smoke in indoor environments. These are the only experiments we are aware of in which the exact number of cigarettes smoked is known and the fate of smoke components on and within complex indoor surface materials are followed for months. In field research, the number of cigarettes and the ventilation conditions are never known precisely. To date, the existing controlled chamber studies of thirdhand smoke do not include smoke exposures this long [50], follow the fate of THS chemicals for as long after the end of the exposure[51] or explore the fate of THS in as many different interior materials. Together, these experiments contribute valuable new information to the study of THS.

Project 5223 and project 5228 appear to have been conceived and executed very rapidly. We did not find the type of comprehensive final reports for them that exist for project 3169 and other major studies that PMI performed in Germany and Belgium. Thus, it is difficult to determine what the people at Phillip Morris thought of the results of their THS studies. However, the assumption stated in the experimental plan, that the chemicals might disappear within a few weeks, was soundly disproven.

Chemical Loss and Surface Materials

The preliminary series of experiments showed that circulation through an unfurnished room with smooth, impermeable epoxy wall paint had a significant effect on smoke chemistry. Total particulate material (TPM), the airborne smoke chemicals that were in a solid or liquid state under the conditions of the experiment, decreased in concentration by 34%. Nicotine decreased by 69%, acrolein by 27% and hydrogen cyanide by 17%, yet the concentrations of ammonia, formaldehyde and acetaldehyde changed by less than 10%. Increasing the surface area of the room by the addition of cloth, wallpaper, carpeting and a bookcase increased the apparent loss of TPM, nicotine, ammonia and formaldehyde, but decreased the losses of acetaldehyde and acrolein from the smoke in the air. These results suggest that the surfaces in a room can affect THS chemistry and that not all THS chemicals respond to increased surface area in the same way. The proportional relationship between surface area and sorption of nicotine and particles, has been observed by several groups since.[51-53] Strictly speaking, the preliminary smoke aging experiments gave no information about the fate of the chemicals that were lost from the smoke. The chemicals could have sorbed and deposited on the surfaces, or they could have reacted to form new chemicals that were not among the limited set that were measured.

Re-Emission into Air

The persistence of chemicals (nicotine, ammonia, formaldehyde and the gas-phase nitrosamine, NPY) in the air of the smoke aging chamber, after 12 hours of ventilation, is strong evidence that these chemicals were either desorbing from the room surfaces or forming through chemical reactions. The concentration of air-borne nicotine (0.31 mg/m^3) was only 40% lower than when fresh smoke was being piped into the room (0.52 mg/m^3). The results for ammonia, formaldehyde and the nitrosamine NPY repeat the pattern of nicotine (Table 1). Later experiments, using both nicotine and cigarette smoke, have shown that nicotine sorbs rapidly to interior surfaces and then re-emits back into the air, [50, 52, 54, 55] and that nicotine can react to form formaldehyde.[56] These are the first data we are aware of on gas-phase nitrosamines in THS.

The concentrations of acetaldehyde in fresh and aged smoke were approximately equal and the concentration decreased from the beginning of the ventilation phase to 12 hours. These results conflict with those of Singer et al., who found acetaldehyde 14 hours after smoking in the air of a room that had been smoked in repeatedly.[50]

Airborne NNK decreased in concentration with aging and was not detectable during the ventilation phase, suggesting that NNK deposited on the surfaces and did not re-emit. The finding that the concentration of cadmium in the particle phase decreases with aging is highly preliminary but suggests that smoking indoors may increase the concentrations of this toxic, heavy metal on indoor surfaces.

Deposition on Surfaces

By extracting nicotine and nitrosamines from surface material samples, PMI closed the loop, proving that nicotine and nitrosamines sorb to common household surfaces and persist in the indoor environment. It is clear that large amounts of nicotine and nitrosamines sorbed to the permeable surfaces in the aging room (carpet, curtain and wallpaper) and were still present after 51 days of ventilation (nicotine and nitrosamines) and 111 days of ventilation (nitrosamines).

Other studies have also shown that nicotine and nitrosamines persist in the indoor environment. Recently, Matt et al. studied NNK levels in the homes of smokers before and after successful cessation. They found that the amount of NNK on wipeable surfaces decreased over time, but the amount of NNK per gram of dust remained the same up to 6 months after cessation.[57] Matt et al. have also measured surface nicotine in homes and found high concentrations of nicotine in homes where no one had smoked for over three years.

By comparing nicotine and nitrosamine concentration in four different materials, Project 5228 also provides entirely new information on how surface chemistry and material structure may affect the chemical reactions occurring in THS. The highest concentrations of nicotine were found in carpet, which has the highest surface area of the four surface materials studied and was on the floor, where larger particles would tend to deposit by gravity. Since NNK appears to form from nicotine in the environment, we would expect the highest concentrations of NNK to be found where the highest concentrations of nicotine were. However, the highest concentrations of NNK were found in the wool curtain, a vertical surface with 9 times less nicotine than carpet. This suggests that something about the wool curtain fabric either promoted the formation of NNK or retarded its breakdown, relative to the wool carpet. This is an entirely new finding and warrants further research.

Chemical Reactions

The mass balance calculation, showing that 60% of the nicotine that entered the system was recovered, yet 170% of the NNK that entered the system was recovered, strongly suggests that NNK was forming in the aging chamber through chemical reactions. In a complex system like the smoke generation and aging system, incomplete recovery of a chemical is more likely than recovery of substantially more chemical than entered the system. These findings are supported by previous publications showing that NNK can form from nicotine both in the air and on surfaces[19, 51, 58]. The finding that the amount of NNK in THS on room surfaces can exceed the amount that was put into the room by smoking is chilling because NNK is one of the most potent carcinogens in tobacco smoke.[59] It will be important to reproduce these findings and to test the effects of aging on other carcinogens like polycyclic aromatic hydrocarbons and 1,3-butadiene.

Limitations

The total number of cigarettes smoked in 105 days (~11,000), represents 1.5 years of exposure in a room where a pack of cigarettes are smoked per day and the smoke concentration in the aging room (9 mg/m^3 TPM inlet, 2.5 mg/m^3 outlet) was substantially higher than the concentrations observed in places where people are actively smoking.[60] The high smoke concentration may have caused higher than normal rates of chemical reactions in the aging chamber. Likewise, the experiment used only sidestream smoke, while real secondhand smoke also contains exhaled mainstream. However, in the real world, people often smoke in a room for decades. Surface wipe samples, collected from smooth surfaces (walls, woodwork and furniture) in a casino one week after a smoking ban, averaged 3 mg/m^2 with a maximum of ~300 mg/m^2. Maximum values observed in the homes of smokers ranged from 1-10 mg/m[61]. The wipe sampling method used in these studies is similar to that used on the glass surfaces in project 5228, where the maximum nicotine concentrations observed were 4.9 mg/m^2. This makes it clear that the nicotine concentrations observed in project 5228 are not a fluke, caused by extreme experimental conditions, but rather represent conditions that can prevail in any room that has been smoked in heavily over a long period of time.

The project 5228 experiments did not have enough samples per time point to permit repeated measures analysis of variance. Our post-hoc analyses of the nicotine data show surface-dependent decreases in concentration over 51 days. The nitrosamine methods were less well-established and the standard deviations were higher than for the nicotine data but there was evidence of trends toward increases in the concentrations of NNK and NNN on painted wallpaper. Recent research has shown that nitrosamines can form on surfaces exposed to smoke and it is likely that NNK was both forming and breaking down into other chemicals. The solvents used to extract nitrosamines for project 5228 were relatively gentle and the data may underestimate the actual concentrations of nicotine and nitrosamines in the samples.

As stated above, the experiments we describe were planned and executed rapidly and their documentation does not include formal summary reports. The Truth Tobacco Documents collection is the result of the documents discovery process during litigation and does not provide a comprehensive representation of the research on THS by the tobacco industry.

Conclusions

This series of well-controlled experiments is the first we are aware of to show that the amount of the carcinogen NNK on surfaces in a smoke-polluted room can exceed the amount that was released into the room by smoking. They also suggest that the chemistry and structure of the surfaces that THS chemicals sorb to can have significant effects on the formation or persistence of nitrosamines in THS. They provide further evidence that THS remains in indoor environments for months, that it re-emits from surfaces back into the air and that it can react to form new toxins and pollutants. Recent research has shown that cleaning does not fully remove THS from surfaces.[57] Treatment with ozone, which anecdotal data suggest is used in hotels[62, 63], is likely to increase the concentration of NNK on surfaces by promoting nitrosation of sorbed nicotine. Disclosure of smoking history in property sale and rental transactions will allow consumers to avoid potential exposure to THS. Furthermore, because the intensity of thirdhand smoke contamination can vary widely, it is also important to develop simple, widely available methods to identify extreme THS contamination. An over-the-counter wipe test would allow the public to identify highly contaminated buildings and vehicles. Because THS is toxic and persistent and because there are no methods known to remove THS pollution, comprehensive smoke free policies are crucial to prevent THS contamination of homes, vehicles and public places.

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