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Characterization of Formaldehyde Exposure Resulting from the Use of Four Professional Hair Straightening Products

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An exposure simulation study was conducted to characterize potential formaldehyde exposures of salon workers and clients during keratin hair smoothing treatments. Four different hair treatment brands (Brazilian Blowout, Coppola, Global Keratin, and La Brasiliana) were applied to separate human hair wigs mounted on mannequin heads. Short-term (6–16 min) and long-term (41–371 min) personal and area samples (at distances of 0.5 to 3.0 m from the source) were collected during each treatment for the 1-day simulation. A total of 88 personal, area, and clearance samples were collected. Results were analyzed based on task sampling (blow-dry, flat-iron), treatment sampling (per hair product), and time-weighted averages (per hair treatment, four consecutive treatments). Real-time monitoring of tracer gas levels, for determining the air exchange rate, and formaldehyde levels were logged throughout the simulation. Bulk samples of each hair treatment were collected to identify and quantify formaldehyde and other chemical components that may degrade to formaldehyde under excessive heat. Mean airborne concentrations of formaldehyde ranged from 0.08–3.47 ppm during blow-dry and 0.08–1.05 ppm during flat-iron. During each treatment, the mean airborne concentrations ranged from 0.02–1.19 ppm throughout different zones of the salon. Estimated 8-hr time-weighted averages for one treatment per day ranged from 0.02 ppm for La Brasiliana to 0.08–0.16 ppm for Brazilian Blowout. For four treatments per day, means ranged from 0.04–0.05 ppm for La Brasiliana to 0.44–0.75 ppm for Brazilian Blowout. Using all four products in one day resulted in estimated 8-hr time-weighted averages ranging from 0.17–0.29 ppm. Results from bulk sampling reported formaldehyde concentrations of 11.5% in Brazilian Blowout, 8.3% in Global Keratin, 3% in Coppola, and 0% in La Brasiliana. Other products that degrade into formaldehyde were detected in Global Keratin, Coppola, and La Brasiliana. The results of this study show that professional hair smoothing treatments—even those labeled "formaldehyde-free"—have the potential to produce formaldehyde concentrations that meet or exceed current occupational exposure limits.

Keywords beauty salon, Brazilian Blowout, formaldehyde, hair salon, hair straightening

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INTRODUCTION

Formaldehyde is a colorless, reactive, volatile organic compound that is ubiquitous in the environment.[1] Formaldehyde is detectable in ambient air (0.2–47 ppb), drinking water (10–100 μg/L), and raw/natural foods (1–90 ppm).[2,3] Annual global formaldehyde production has been estimated at nearly 21 million tons, and it is used principally in the production of resins to make adhesives and binders (wood products, plastics, textile finishing), as a biocide and preservative (agriculture, medicine, cosmetics), and as an intermediate in certain chemical reactions.[1,2,4] It is estimated that over 2 million American workers have been exposed to formaldehyde, and approximately 50% of those workers are in the garment industry.[1]

Eye irritation is the most sensitive non-cancer health endpoint associated with exposure to airborne formaldehyde, which, for most of the population, occurs at concentrations between 0.1 and 0.5 ppm.[5] Other potential non-cancer health effects range from respiratory irritation and immunological and neurological conditions may occur following acute formaldehyde exposure to reproductive and developmental conditions following intermediate to chronic exposure.[1] Both the U.S. Department of Health and Human Services' National Toxicology Program (NTP) and the International Agency for Research on Cancer (IARC) have classified formaldehyde as a known human carcinogen.[2,6]

Formaldehyde has long been a common ingredient in homemade and professional hair straightening (also referred to as "smoothing") products.[7,8] Hair proteins, known as keratins, are altered by formaldehyde during the treatments to

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prolong the straightening effect in curly hair.[9] The process by which these hair straightening products are used, excluding preparatory tasks (such as shampooing), generally includes the following three tasks: (1) applying product to the hair, (2) blow-drying the hair, and (3) heat treating the hair (generally using a flat iron set at approximately 450°F). In early 2007, professional semi-permanent hair straightening products, which were marketed as "formaldehyde-free," gained widespread acceptance in the U.S. market, primarily as a response to industry and consumer concerns regarding health risks associated with commercial formaldehyde use.

In 2010, in response to complaints (e.g., difficulty breathing, nosebleeds, and eye irritation) in stylists performing hair straightening treatments in the Portland, Oregon, area, the Oregon Occupational Safety and Health Administration (Oregon OSHA) analyzed 105 bulk samples from 12 different hair straightening products and found measurable formaldehyde levels (average: 1.2–8.8%) in nine products (three products contained < 0.01% formaldehyde).[10] Personal air sampling was conducted at seven salons during the use of Brazilian Blowout Acai Professional Smoothing Solution (referred to herein as Brazilian Blowout), a product that is labeled as "formaldehyde-free." In general, the lowest "task-based" (6–48 min) concentrations were reported during product application (range: 0.206–1.26 ppm, mean = 0.590 ppm); somewhat higher levels were measured during flat-ironing (range: 0.181–1.35 ppm, mean = 0.543 ppm) and blow-drying (range: 0.176–1.88 ppm, mean = 0.995 ppm). Treatment-based time-weighted average (TWA) concentrations (i.e., the average concentration of formaldehyde throughout the course of one treatment [45–114 min]) ranged from 0.059 to 1.39 ppm. In addition, 8-hr TWA formaldehyde concentrations calculated for each stylist ranged from 0.006 to 0.331 ppm.

In May 2011, the National Institute for Occupational Safety and Health (NIOSH) released the results from a Health Hazard Evaluation (HHE) conducted in December 2010.[11] NIOSH collected short-term, task-based air samples at a hair salon in Ohio during a single hair straightening treatment with the Brazilian Blowout solution. Formaldehyde concentrations were found to range from 0.018–1.3 ppm (n = 12). Analysis of bulk sampling indicated that Brazilian Blowout contained 11% formaldehyde by weight.[11]

None of the airborne formaldehyde concentrations measured by Oregon OSHA or NIOSH exceeded the OSHA 15-min short-term exposure limit (STEL) of 2 ppm, nor did the estimated 8-hr TWA values exceed the 8-hr permissible exposure limit (PEL) of 0.75 ppm. However, these studies evaluated only the use of a single product (Brazilian Blowout) during a single treatment. In reality, numerous treatments with multiple products might occur in a given salon throughout the day, and therefore, these data may not be representative of a full workday exposure. Also, only personal samples were collected, and therefore, potential occupational bystander (e.g., stylist working at the adjacent chair, receptionist) and non-occupational (e.g., treatment customer, customers in waiting room) exposures cannot be easily evaluated from the available data. Finally, the rate at which formaldehyde dissipates throughout the indoor air of a salon is dependent on the salon's dimensions and air exchange rates, which were not reported in either study, making it difficult to extrapolate the data to other working salons.

Hairdressers and allied professionals represent a large and fast-growing occupational group, with over 630,000 current employees and a projected 20% growth in the work force by 2018.[12] Given the limited sampling data available, an independent investigation of the potential formaldehyde exposures resulting from the use of hair straightening products was conducted. In this study, levels of airborne formaldehyde associated with the use of four commonly used hair straightening products (including Brazilian Blowout) were measured. Short-term samples and longer-term samples were collected under simulated conditions involving an actual hair salon and a professional stylist. Samples were collected at locations representative of the stylist performing the treatment, the customer receiving the treatment, and at bystander and more remote locations. The airborne data are characterized via comparisons to short-term and long-term occupational standards and the measurements previously reported by Oregon OSHA and NIOSH. The data were also evaluated for trends regarding airborne formaldehyde levels as a function of (1) formaldehyde concentrations in the original product, (2) specific treatment tasks (e.g., blow-drying vs. flat-ironing), and (3) distance from the stylist. In addition to the bulk analyses conducted to determine the product concentration of formaldehyde, other chemicals in the parent products that could thermally decompose into formaldehyde were quantified.

METHODS

Study Protocol

The study was conducted during a single day in June 2011, in a 260-m^3 hair salon in downtown Chicago, Illinois. The size of the actual treatment room was about 140 m^3 and contained 14 hair styling stations (hereafter referred to as chairs), arranged in sets of seven along two long walls (Figure 1). Sampling was conducted during the use of four commercially available hair smoothing products marketed for professional use (Coppola Keratin Complex Blonde Formula [Coppola], Global Keratin Juvexin Optimized Functional Keratin [Global Keratin], La Brasiliana Escluso Keratin Treatment with Collagen [La Brasiliana], and Brazilian Blowout Acai Professional Smoothing Solution [Brazilian Blowout]). Each product was tested separately in a random order. All products were applied to professional human hair wigs (approximately shoulder length (Figure 2), which were purchased mounted on mannequin heads) in a manner consistent with their respective manufacturer's recommendations. While the recommendations differed somewhat among the products (e.g., task durations), the general application process can be characterized as follows:

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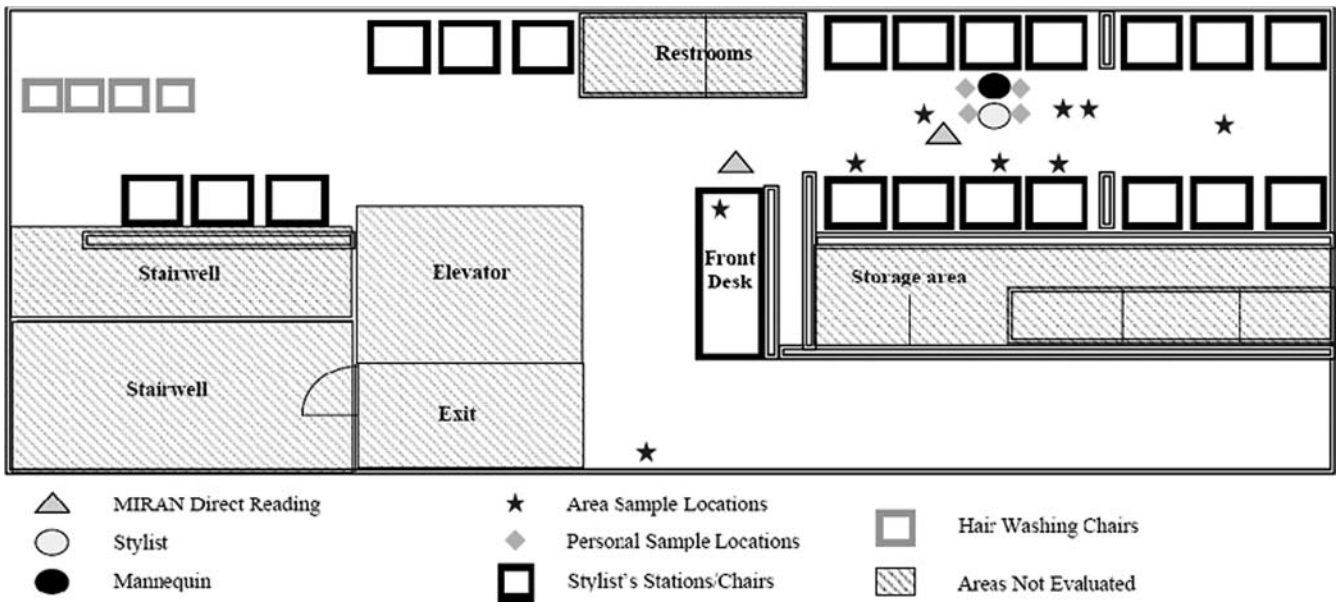

FIGURE 1. Map of salon including workstations and sampling locations.

- Preparatory work: Hair was washed and dried until damp.
- *Task 1. Application.* This task involved sectioning the hair using a comb and clips and applying about 2 ounces of product using an application brush. On average, this task took 10 min. One product (Coppola) required a 20-min processing period following application (per the manufacturer's instructions).
- *Task 2. Blow-Dry.* Hair was dried using a hand-held blow dryer and a round brush. On average, this task took 9 min.
- *Task 3. Flat-Iron.* This task first involved sectioning the hair using a comb and clips. Each section was flat-ironed multiple times using a small and a large flat iron, both set at 450°F. On average, this task took 26 min.

FIGURE 2. Example of professional human hair wig.

The hair treatments were considered complete after the styling tools were cleaned at a distant sink station and put away.

Sampling and Analytical Methods

Air samples were collected at the stylist, consumer (mannequin heads), bystander (area), and remote (area) locations; a schematic of these locations is presented in Figure 1. Treatment-duration and task-duration personal active samples were collected on the right and left lapels (breathing zone) of the stylist and corresponding locations relative to the mannequin head during each of the four hair treatments. Five active area samples were collected at breathing zone height (1.5 m) at locations 0.5 to 1 m and 2 to 3 m away from the stylist's work area (to the right, left, and behind the stylist). These samples were intended to represent potential bystander exposures during treatments, and the locations corresponded to the adjacent workstations. An additional two, active area samples were collected in the reception area and were intended to represent potential remote exposures. Personal passive samples were collected on the right and left lapels of the stylist, at all five bystander locations, and one remote location over the full day of the study (approximately 6 hr). In addition, an active 15-min clearance sample was collected at breathing zone height on the right side of the stylist's workstation before each treatment began. The four clearance samples were intended to represent

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the background formaldehyde concentrations prior to each treatment sampling period (they were collected immediately before each treatment). The first clearance sample was considered to be representative of the background concentration in the salon.

All airborne active samples for formaldehyde were collected on 2,4-dinitrophenylhydrazine (DNPH) Silica Gel sorbent tubes (catalog number 226-119, SKC Inc., Eighty Four, Pa.), using SKC AirChek 52 Air Sample pumps (SKC) attached with special low flow adaptors. Active samples collected during the duration of each treatment (personal and area) were collected at an airflow rate of approximately 0.1 L/min for approximately 1 to 1.5 hr. Additional short-term (15 min) personal samples were collected at an airflow rate of approximately 0.3 L/min during the latter two tasks detailed above (i.e., blow-drying and flat-ironing). Blank DNPH tubes were provided to the lab for quality control purposes; formaldehyde-spiked tubes were not provided to the laboratory for analysis. The sampling pumps were calibrated with a Bios DryCal DC-Lite primary flow calibrator (Bios International Corporation, Butler, N.J.) before and after sample collection.

Passive samples for formaldehyde were collected for the duration of the full sampling day using N571 Aldehyde Passive Monitors (Assay Technology, Livermore, Calif.). Blank passive monitors were provided to the lab for quality control purposes; formaldehyde-spiked samples were not provided to the laboratory for analysis. Sample collection equipment, materials, and procedures were consistent with NIOSH Method 2016.[13]

All sampling media were sealed immediately after each sampling event, packaged with freezer ice packs, and sent for overnight delivery to an AIHA® -accredited laboratory. All airborne samples were analyzed by a modified NIOSH Method 2016 using high performance liquid chromatography (HPLC) and ultraviolet (UV) detection.[13]

Real-time airborne measurements of formaldehyde (0.5 s in length) were logged using a MIRAN 205B Series SapphIRe portable ambient air analyzer (Thermo Electron Corporation Environmental Instruments, Franklin, Mass.) before, during, and after all hair treatment applications. Concentrations were recorded at the stylist's workstation (Zone 1) and near the reception area (Zone 4) every 5 min.

Bulk Sample Collection and Analysis

Two 25-mL bulk samples of three of the hair treatment products were collected in glass vials before the treatments commenced; due to a limited amount of the Coppola Keratin Complex, only 10 mL of this product was collected for bulk analysis. All bulk samples were sent to a lab for identification and quantification of formaldehyde, methylene glycol, propylene glycol, and cyclopentasiloxane. Formaldehyde was identified and quantified using a modified NIOSH 3500 method.[14] Methylene glycol, propylene glycol, and cyclopentasiloxane were identified and quantified using gas chromatography and mass spectrometry with Restek chemical standards.[15,16]

Ventilation

The salon's ventilation system was a forced air system. Since the study was conducted on a warm day (average outdoor temperature = 78°F), the building's air conditioning was operating, introducing cool dry air into the salon. Indoor temperature and relative humidity were measured at the beginning of the sampling day using a portable temperature and humidity monitor. The salon had no local exhaust ventilation. The front door, the only entrance to the salon, was kept shut for the entire duration of the study.

Sulfur hexafluoride (SF_6), an inert, odorless, colorless and nontoxic gas, was used as a tracer gas to estimate the rate of air exchange within the salon. Measurements of the gas were taken according to ASTM method E741–00(2006)e1 using an additional MIRAN 205B Series SapphIRe portable ambient air analyzer (Thermo Electron). A target concentration of about 4 ppm for SF_6 (assay ≥99.75%, Sigma-Aldrich, St. Louis, Mo.) was chosen based on the detection range of the sampling instrument. Given the volume of the salon, one 1-L Tedlar bag (Fisher Scientific, Hampton, N.H.) was filled with SF_6 in a separate location from the salon to prevent inadvertent release inside the salon. The contents of the Tedlar bag were emptied throughout the salon with all exterior and interior doors closed, and two fans located at opposite ends of the salon were turned on for 5 min to facilitate even dispersion of the gas.

Air measurements were collected at eight evenly spaced locations throughout the salon using the MIRAN analyzer, beginning 1 min after the release of the SF_6 and until steady-state was reached (i.e., consecutive measurements showed a difference of no greater than 10%). The steady-state concentration was approximately 1.13 ppm. Once steady-state was confirmed, measurements were collected and logged at one central location, every 2.5 to 5 min for approximately 2 hr. Assuming constant air change, the air exchange rate was calculated by performing a linear regression on the following equation:

$$\ln C_t = -A \times t + \ln C_0$$

where t corresponds to time in hours (after the steady-state is achieved), C_t represents concentration at time t, and C_0 was the initial concentration.

The air exchange rate in the salon was determined to be 2.41 hr^{-1}, which is consistent with previous studies in salon settings.[17]

Study Participants

Hair treatments were performed by a licensed cosmetologist (referred to hereafter as the "stylist"), who routinely performs hair straightening treatments. Before sampling began, the stylist and investigators involved in implementing the study received training regarding the possible hazards of working in environments containing formaldehyde.[6,18] In addition, the stylist and investigators were fit-tested and wore half-face NIOSH-approved respirators (3M 6000 series with formaldehyde/organic vapor cartridges, 3M, St. Paul, Minn.) during the treatments. IRB approval was obtained from a

medical institutional review board that was in compliance with the federal regulations of the National Institutes of Health, the Office of Human Research Protections, and the Food and Drug Administration, and was accredited by the National Committee for Quality Assurance (Protocol number: CR_CHI-001; Essex Institutional Review Board, Inc., Lebanon, N.J.).

Data Analysis

For purposes of performing statistical comparisons of airborne concentrations at different sampling locations, the sampling data were grouped into four zones. Zone 1 encompassed sampling locations within the vicinity of the treatment site (i.e., the samples collected within the breathing zones of the stylist and the mannequin). Zone 2 included sampling locations within 0.5 to 1 m of the treatment site (i.e., the samples collected at the adjacent workstations). Zone 3 included sampling locations within 2 to 3 m of the treatment site (i.e., the samples collected at distant workstations), and Zone 4 consisted of the samples collected within 6 to 10 m of the treatment site (i.e., the samples collected in the reception area). All statistical procedures were performed using commercial statistical software (SAS version 9.2; SAS Institute Inc., Cary, N.C.).

To identify differences in mean airborne formaldehyde concentration among zones and products, the SAS procedure PROC MIXED was utilized to account for correlation between repeated measures in lieu of typical ANOVA analysis procedures that rely on the assumption of independence between measurements.[19] For each product, Student's t-tests were computed using the SAS procedure PROC TTEST to assess differences in mean formaldehyde concentration between individual zones. A test for equality of variances between two zones was conducted using the Folded F statistic. If evidence of unequal variances was found, the Satterthwaite test was used to calculate the test statistic. Otherwise, equal variances were assumed, and the test statistic was computed using a pooled standard deviation. To evaluate differences in mean formaldehyde concentration between products, a paired t-test with observations matched on zone location was performed.

Using the SAS procedure PROC REG, linear regression analyses were also performed to characterize the effects of selected exposure variables on the measured airborne formaldehyde concentrations, such as bulk concentrations of several chemicals in the products, and task durations.

Because real-time measurements were taken in Zones 1 and 4 in 5-min intervals for each treatment, there were several real-time measurements that corresponded to each 15-min task-based sample. For this reason, the real-time measurements were time-weighted according to pump sampling times to ensure comparison over the same sampling period. A linear regression analysis was then performed using SAS's PROC REG, whereby the active sampling data were assumed to the response variable (Y), and the real-time data were assumed to be the regressor variable (X), as another means of validating the results.

Estimation of Time-Weighted Average Exposures

Treatment-based TWAs for each zone were derived from the average of the treatment-duration samples collected in each zone. Subsequently, 8-hr TWA formaldehyde concentrations were calculated for each zone using the treatment-based TWAs for three different exposure scenarios:

- *Scenario 1*. TWAs were calculated under the assumption that only one treatment was performed during an 8-hr workday (Eq. 1). The treatment-based TWA for product *x* and location *k* ($TWA_{x,k}$, $1 \leq x \leq 4$, $1 \leq k \leq 4$) was used for the treatment duration (t_x, in minutes). It was assumed that the concentration for the 15-min period after the treatment was equal to the clearance concentration measured after that particular treatment ($C_{clear,y}$), where y corresponds to the interval of time between treatments. For the last product, La Brasiliana, the treatment-specific TWA was very low, and the initial background concentration was used for the remaining time (e.g., $C_{clear,3} = C_{backgr}$). For the remainder of the time it was assumed that the concentration was equal to the concentration measured before the first treatment (i.e., the first clearance sample that was assumed to represent the background concentration, C_{backgr}).

$$TWA_{1,x,k} = \frac{TWA_{x,k} \times t_x + C_{clear,y} \times 15 + C_{backgr} \times (480 - 15 - t_x)}{480} \quad (1)$$

- *Scenario 2*. TWAs were calculated assuming that four treatments using the same product were performed during one 8-hr workday (Eq. 2). It was assumed that the treatment began 15 min after the beginning of the 8-hr time period considered. The TWA for each product and zone ($TWA_{x,k}$) was multiplied by the treatment duration (t_x) (as measured during our study), and the number of treatments ($n = 4$). We assumed that the initial concentration (i.e., prior to the first treatment) was equal to the concentration measured before the first treatment (C_{backgr}). The concentration for the remaining time was assumed to be equal to the clearance concentration measured after that particular treatment ($C_{clear,y}$), where y corresponds to the interval of time between treatments. This assumption may have resulted in an underestimate of the exposure since the background concentration of formaldehyde would be expected to increase with each successive treatment. For the last product, La Brasiliana, the treatment-specific TWA was very low, and the initial background concentration was used for the remaining time (e.g., $C_{clear,3} = C_{backgr}$).

$$TWA_{2,x,k} = \frac{4 \times TWA_{x,k} \times t_x + C_{backgr} \times 15 + C_{clear,y} \times (480 - 15 - 4t_x)}{480} \quad (2)$$

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- *Scenario 3*. TWAs were calculated under assumptions that mirrored the actual conditions during the simulation study (Eq. 3). It was assumed that the four products were used in the same order in which they were used in the study and that the concentrations for the time period between the treatments (t_y, $1 \leq y \leq 3$) was equal to the corresponding clearance concentration ($C_{clear,y}$). The initial background concentration was assumed for the remaining duration of the workday, i.e., the difference between 8 hr and the duration of the total study.

$$TWA_{3,k} = \frac{\sum_{x=1}^{4}\left(TWA_{x,k} \times t_x\right) + \sum_{y=1}^{3}\left(C_{clear,y} \times t_y\right) + C_{backgr} \times \left\{480 - \left(\sum_x t_x + \sum_y t_y\right)\right\}}{480} \quad (3)$$

RESULTS

Airborne Formaldehyde Concentrations

A total of 88 samples were collected and analyzed for formaldehyde during the four treatments, consisting of 36 short-term (32 task duration, and 4 clearance), 44 long-term (treatment duration), and 8 long-term (full-day) samples.

Task-Based Sampling

The mean airborne concentrations of formaldehyde ranged from 0.08 to 2.35 ppm and 0.11 to 3.47 ppm during blow-drying and 0.08 to 1.11 and 0.08 to 1.05 ppm during flat-ironing, for the stylist and the mannequin, respectively (Table I). Only one sample, collected in the stylist's breathing zone during the blow-drying task of the La Brasiliana treatment, was below the analytical LOD (< 0.05 ppm). For purposes of performing statistical comparisons, the concentration for this sample was assumed to be one-half the LOD. A comparison of the task-based sampling data for the individual treatments is presented in Figure 3.

Statistical comparisons of the task-based sampling results are presented in Table II. Regarding sample location, mean formaldehyde levels measured in the stylist's vs. the mannequin's breathing zones were not significantly different during flat-ironing. During Brazilian Blowout blow-drying, the mean levels measured in the mannequin's breathing zone (3.47 ppm) were significantly higher than in the stylist's breathing zone (2.35 ppm) ($p = 0.01$), which greatly affected the overall stylist-mannequin comparison during blow-drying in which the mean formaldehyde levels in the two locations were found to be different ($p = 0.0005$). During blow-drying, all treatments were found to have statistically significantly different mean levels of airborne formaldehyde from one another: Brazilian Blowout > Global Keratin > Coppola> La Brasiliana (all $p < 0.05$) (Table II). During flat-ironing, all treatments were found to have statistically significantly different mean levels of airborne formaldehyde from one another, with the exception of Coppola and La Brasiliana (Brazilian Blowout > Global Keratin > Coppola and La Brasiliana, all $p < 0.003$) (Table II). Also, for any given product the mean formaldehyde concentrations measured during blow-drying were higher (sometimes statistically significantly higher) than those measured during flat-ironing. Again, this was true for both the stylist and mannequin samples.

As shown in Table III and Figure 3, for some products, the formaldehyde concentrations measured in the breathing zone of the stylist or the mannequin during the blow-drying and flat-ironing tasks exceeded the NIOSH 15-min REL-C of 0.1 ppm (Coppola, Brazilian Blowout, and Global Keratin), the ACGIH® threshold limit value-ceiling (TLV-C) of 0.3 ppm (Brazilian Blowout and Global Keratin), and the 15-min OSHA STEL of 2 ppm (Brazilian Blowout, blow-drying only) (Figure 3).

TABLE I. Task-Based Airborne Formaldehyde Concentrations (ppm) Associated with the Blow-Dry and Flat-Iron Tasks

		Stylist				Mannequin			
Treatment[A]	Task	Number of Samples	Sample Duration (min)	Mean Concentration (ppm)	Range (ppm)	Number of Samples	Sample Duration (min)	Mean Concentration (ppm)	Range (ppm)
Coppola	Blow-dry	2	15	0.19	0.18–0.19	2	15	0.21	0.2–0.22
	Flat-iron	2	15	0.11	0.09–0.13	2	15	0.10	0.09–0.11
Brazilian Blowout	Blow-dry	2	10	2.35	2.29–2.41	2	10	3.47	3.36–3.59
	Flat-iron	2	13	1.11	0.96–1.26	2	13	1.05	1.05–1.05
Global Keratin	Blow-dry	2	8	1.62	1.48–1.76	2	8	1.68	1.58–1.78
	Flat-iron	2	16	0.53	0.52–0.55	2	16	0.52	0.51–0.53
La Brasiliana	Blow-dry	2	6	0.08[B]	< 0.05–0.14	2	6	0.11	0.09–0.14
	Flat-iron	2	15	0.08	0.08–0.09	2	15	0.08	0.08–0.09

[A]Listed in the order treatments were performed.
[B]Used 1/2 LOD when calculating the average concentration.

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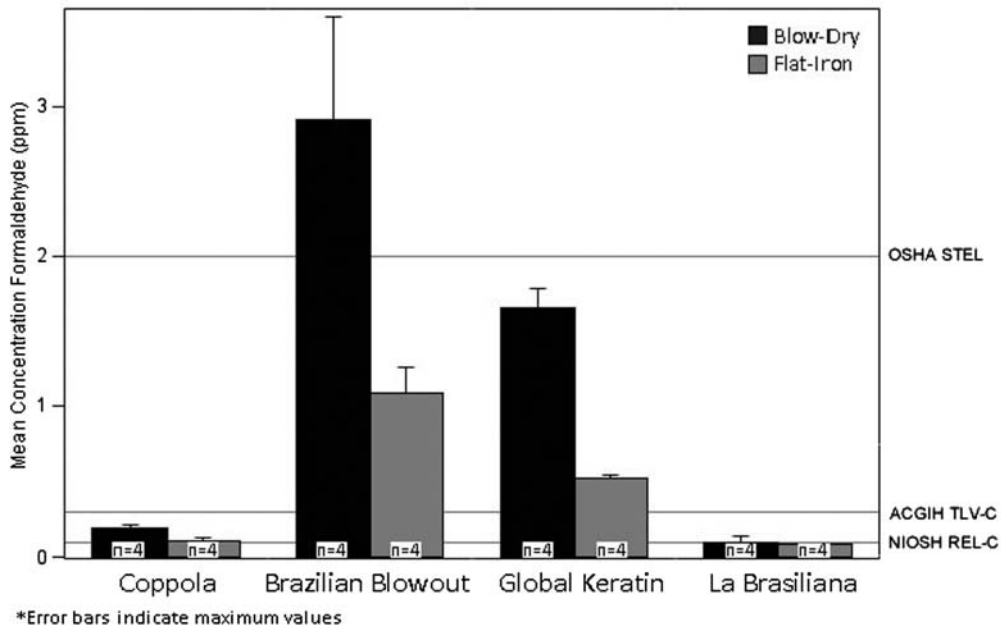

FIGURE 3. Comparison of task-based concentrations (ppm) to current occupational exposure limits (OELs) for formaldehyde.

Treatment-Based Sampling

The means of the formaldehyde concentrations measured in Zones 1 through 4 for the treatment-duration samples are summarized in Table IV. A comparison of the treatment-based sampling data for the individual treatments is presented in Figure 4.

The statistical comparisons of the sampling results for the various zones, by treatment, are presented in Table V. Two trends are apparent in these data. First, the overall mean formaldehyde concentrations measured in each zone (for all treatments combined) decreased significantly with increasing distance from the stylist (Zone 1 > Zone 2 > Zone 3 >

TABLE II. Statistical Comparisons of Task-Based Sampling Results for the Stylist and the Mannequin, and by Treatment

				Treatment[C]			
Task	**Overall[A]**	**Treatment**	**Stylist vs. Mannequin[B]**	**Coppola**	**Brazilian Blowout**	**Global Keratin**	**La Brasiliana**
All	N(0.086)	Coppola	N (1.00)	—	Y (<0.0001)	Y (<0.0001)	N (0.66)
		Brazilian Blowout	N (0.30)	—	—	Y (<0.0001)	Y (<0.0001)
		Global Keratin	N (0.32)	—	—	—	Y (<0.0001)
		La Brasiliana	N (0.50)	—	—	—	—
Blow-dry	Y(0.0005)	Coppola	N (0.16)	—	Y (0.0034)	Y (0.0002)	Y (0.048)
		Brazilian Blowout	Y (0.01)	—	—	Y (0.026)	Y (0.0031)
		Global Keratin	N (0.75)	—	—	—	Y (0.0005)
		La Brasiliana	N (0.64)	—	—	—	—
Flat-iron	N(0.93)	Coppola	N (0.68)	—	Y (0.0004)	Y (<0.0001)	N (0.15)
		Brazilian Blowout	N (0.74)	—	—	Y (0.0022)	Y (0.0006)
		Global Keratin	N (0.55)	—	—	—	Y (<0.0001)
		La Brasiliana	N (0.91)	—	—	—	—

Note: N = no statistically significant difference observed; Y = statistically significant difference observed; number in parentheses corresponds to p-value.
[A]Test of the null hypothesis: the pattern of change for mean formaldehyde concentration was the same for all products (PROC MIXED).
[B]Test of the null hypothesis: $\mu_{stylist} - \mu_{mannequin} = 0$ (paired t-test on zone location).
[C]Test of the null hypotheses: $\mu_{trt1} - \mu_{trt2} = 0, \ldots, \mu_{trt3} - \mu_{trt4} = 0$ (paired t-test on zone location).

TABLE III. Current Occupational Exposure Limits (OELs) for Formaldehyde

Agency	OEL	Averaging Time	Concentration (ppm)
OSHA	PEL	8 hr	0.75
	AL	8 hr	0.5
	STEL	15 min	2
NIOSH	REL	8 hr	0.016
	REL-C	15 min	0.1
ACGIH	TLV-C	Ceiling	0.3

Zone 4; $p < 0.0001$). This pattern generally held true for the individual products as well, with the exception of the La Brasiliana product (no significant difference between any of the zones).

Second, for any given zone, the mean formaldehyde concentrations followed a consistent pattern: Brazilian Blowout > Global Keratin > Coppola and La Brasiliana (all $p < 0.0001$ with the exception of Coppola and La Brasiliana, which were not statistically different). This is consistent with the mean concentration trend observed for the task-based samples.

As shown in Table IV and Figure 4, the mean formaldehyde concentrations measured in Zones 1 through 4 during the Brazilian Blowout and Global Keratin treatments exceeded the short-term REL-C and TLV-C values. Mean concentrations measured during the Coppola and La Brasiliana treatments were generally below the short-term limits. None of the samples exceeded the OSHA STEL.

Background and Clearance Sampling

As shown in Table IV, the background formaldehyde concentration in the salon, measured prior to the first treatment, was less than the LOD (< 0.02 ppm). Formaldehyde concentrations for the three clearance samples ranged from 0.03 ppm to 0.32 ppm and were consistent with the formaldehyde levels measured during the prior treatment (e.g., post-Brazilian Blowout had the highest clearance measurement). This pattern is also reflected in the real-time data presented in Figure 5.

Full-Shift Sampling

Mean airborne formaldehyde concentrations for the passive samples collected throughout all four treatments (371 min) ranged from 0.25 ppm in the reception area (Zone 4) to 0.43 ppm for the stylist (Zone 1, Table VI). A comparison of the passive sampling data for the individual zones is presented in Figure 4, which shows that the mean formaldehyde concentrations in all zones were above the NIOSH REL and REL-C but below the OSHA PEL. In addition, full-day samples collected in Zones 1 and 2 were above the ACGIH TLV-C.

Real-Time Monitoring

As can be seen in Figure 5, the real-time measurements (obtained in Zones 1 and 4) followed the trends observed for the task- and treatment-based, and the full-shift data. Specifically, (1) formaldehyde levels in Zone 1 > Zone 4, (2) the Brazilian Blowout treatment was associated with the highest formaldehyde levels, while La Brasiliana treatment was associated with relatively low concentrations, and (3) formaldehyde levels were highest during the blow-drying task. The ACGIH TLV-C was exceeded for all products except La Brasiliana. As shown in Figure 6, the real-time measurements were highly correlated with the active sampling data ($R^2 = 0.88$). The slope and intercept for the regression model were 1.12 and 0.04, respectively (SD = 0.08, p = 0.66).

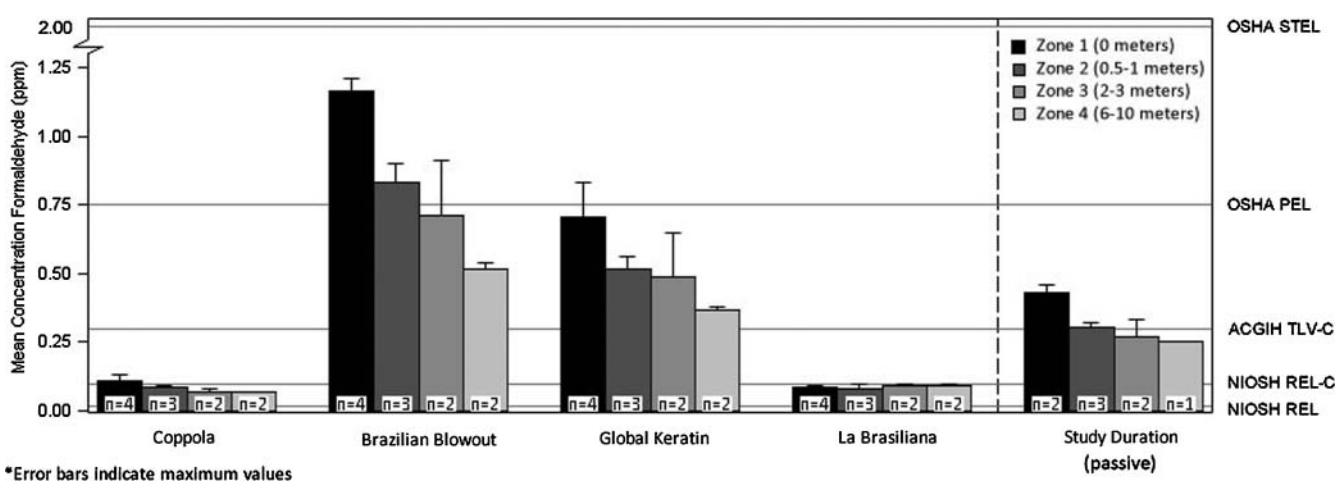

FIGURE 4. Comparison of treatment-based and full-shift concentrations (ppm) to current occupational exposure limits (OELs) for formaldehyde.

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TABLE IV. Treatment-Duration Airborne Formaldehyde Concentrations (ppm) Associated with Professional Hair Straightening Treatments

Treatment	Sampling Location[A]	Distance from Stylist (m)	Number of Samples	Sample Duration (min)	Mean Concentration (ppm)	Range (ppm)
Coppola						
	Background	0	1	15	< 0.02	
	Zone 1	0	4	82–84	0.11	0.09–0.13
	Zone 2	0.5–1	3	83	0.09	0.08–0.09
	Zone 3	2–3	2	83	0.07	0.06–0.08
	Zone 4	6–10	2	84	0.07	0.07–0.07
Brazilian Blowout						
	Clearance	0	1	15	0.03	
	Zone 1	0	4	56–57	1.17	1.13–1.21
	Zone 2	0.5–1	3	55	0.83	0.72–0.90
	Zone 3	2–3	2	55	0.71	0.51–0.91
	Zone 4	6–10	2	56	0.52	0.49–0.54
Global Keratin						
	Clearance	0	1	15	0.32	
	Zone 1	0	4	50	0.71	0.58–0.83
	Zone 2	0.5–1	3	50	0.52	0.45–0.56
	Zone 3	2–3	2	50	0.49	0.33–0.65
	Zone 4	6–10	2	51	0.37	0.36–0.38
La Brasiliana						
	Clearance	0	1	15	0.17	
	Zone 1	0	4	41	0.03	0.02–0.03
	Zone 2	0.5–1	3	41	0.02	0.02–0.03
	Zone 3	2–3	2	41	0.03	0.02–0.03
	Zone 4	6–10	2	41	0.03	0.02–0.03

[A]Zone 1: 0 m, Zone 2: 0.5–1.0 m, Zone 3: 2.0–3.0 m, Zone 4: 6–10 m.

Estimated Time-Weighted Average Concentrations

Consistent with the trends observed in the measured data, the estimated TWAs for each of the three exposure scenarios appeared to decrease with increasing distance from the treatment location, and airborne formaldehyde levels in any given zone followed the same pattern: Brazilian Blowout > Global Keratin > Coppola > La Brasiliana (Table VII). For Scenario 3, the duration that was used to account for the time between the first and second, second and third, and third and fourth treatments was 62, 40, and 34 min, respectively, which corresponded to the actual durations between the successive treatments. All of the estimated TWAs exceeded the NIOSH REL, none of the TWAs exceeded the OSHA PEL (although the estimated TWA for Brazilian Blowout in Scenario 2 was equal to the OSHA PEL). The NIOSH REL-C was exceeded in Scenario 1 for Brazilian Blowout in Zones 1 and 2 only. For Scenario 2, the NIOSH REL-C was exceeded in all zones for Brazilian Blowout and Global Keratin, as was the ACGIH TLV-C for all zones and Zones 1 and 2, for the two treatments, respectively. The NIOSH REL-C was exceeded in all zones in Scenario 3. The results for the passive air sampling were not found to be different from the estimated TWAs using assumptions based on Scenario 3 ($p = 0.62$).

Limits of Detection

Based on the sampling volumes, the limit of detection (LOD) for short-term active samples (task-based and clearance) ranged from 0.021 mg/m^3 (0.017 ppm) to 0.055 mg/m^3 (0.045 ppm). The LOD ranged from 0.012 mg/m^3 (0.010 ppm) to 0.024 mg/m^3 (0.020 ppm) for the 84-min to 41-min samples (treatment based). For the passive samples, the LOD ranged from 0.020 mg/m^3 (0.017 ppm) to 0.024 mg/m^3 (0.019 ppm). Concentrations were not adjusted for the background levels of formaldehyde in the ambient air because all measurements taken immediately before the commencement of each treatment yielded airborne chemical concentrations below the LOD of the direct-reading equipment (MIRAN analyzer's LOD for formaldehyde = 0.11 ppm). The NIOSH REL of 0.016 ppm is below the LODs employed in this study.

Bulk Sample Analysis

Brazilian Blowout was found to have a mean formaldehyde concentration of 11.5% (115.1 mg/mL), 8.3% (82.8 mg/mL)

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TABLE V. Statistical Comparisons of Treatment-Based Sampling Results for the Various Zones, by Treatment

Treatment	Overall[B]	Zone[C]	Zone[A] 1	2	3	4
All	Y (< 0.0001)	1	—	N (0.40)	N (0.35)	N (0.076)
		2	—	—	N (0.80)	N (0.39)
		3	—	—	—	N (0.57)
		4	—	—	—	—
Coppola	Y (0.016)	1	—	N (0.068)	Y (0.043)	Y (0.016)
		2	—	—	N (0.15)	Y (0.038)
		3	—	—	—	N (1.00)
		4	—	—	—	—
Brazilian Blowout	Y (0.0021)	1	—	Y (0.0013)	N (0.26)	Y (< 0.0001)
		2	—	—	N (0.51)	N (0.025)
		3	—	—	—	N (0.44)
		4	—	—	—	—
Global Keratin	Y (0.047)	1	—	Y (0.037)	N (0.16)	Y (0.012)
		2	—	—	N (0.85)	N (0.045)
		3	—	—	—	N (0.53)
		4	—	—	—	—
La Brasiliana	N (0.94)	1	—	N (0.79)	N (0.63)	N (0.63)
		2	—	—	N (0.73)	N (0.73)
		3	—	—	—	N (1.00)
		4	—	—	—	—

Note: N = no statistically significant difference observed, Y = statistically significant difference observed; number in parentheses corresponds to p-value.
[A]Test of the null hypotheses: $\mu_{trt1} - \mu_{trt2} = 0, \ldots \mu_{trt3} - \mu_{trt4} = 0$ (paired t-test on zone location).
[B]Test of the null hypothesis: the pattern of change for mean formaldehyde concentration was the same for each zone (PROC MIXED).
[C]Zone 1: 0 m; Zone 2: 0.5–1.0 m; Zone 3: 2.0–3.0 m; Zone 4: 6–10 m.

formaldehyde was found in Global Keratin, and Coppola consisted of 3% (29.9 mg/mL) formaldehyde. The concentration of formaldehyde in La Brasiliana was below the LOD (< 0.5 μg/mL, corresponding to 5×10^{-7}% by weight). The mean cyclopentasiloxane concentration was 0.3% (2.5 mg/mL) in Global Keratin, 0.4% (3.8 mg/mL) in Coppola, and below the LOD (< 5.0 μg/mL, corresponding to 5×10^{-6}% by weight) in Brazilian Blowout and La Brasiliana. Propylene glycol was only detected in La Brasiliana at a mean concentration of 0.38% (3.8 mg/mL). Methylene glycol was not detected in any of the four products.

Using univariate analysis, the concentration of formaldehyde in each product was found to be a significant predictor of the airborne concentration of airborne formaldehyde

TABLE VI. Full-Shift Airborne Formaldehyde Concentrations (ppm) Associated with Professional Hair Straightening Treatments

Sampling Location[A]	Distance from Stylist (m)	Number of Samples	Sample Duration (min)	Mean Concentration (ppm)	Range (ppm)
Zone 1	0	2	371	0.43	0.40–0.46
Zone 2	0.5–1	3	371	0.31	0.28–0.32
Zone 3	2–3	2	371	0.27	0.21–0.33
Zone 4	6–10	1	371	0.25	0.25–0.25

[A]Zone 1: 0 m, Zone 2: 0.5–1.0 m, Zone 3: 2.0–3.0 m, Zone 4: 6–10 m.

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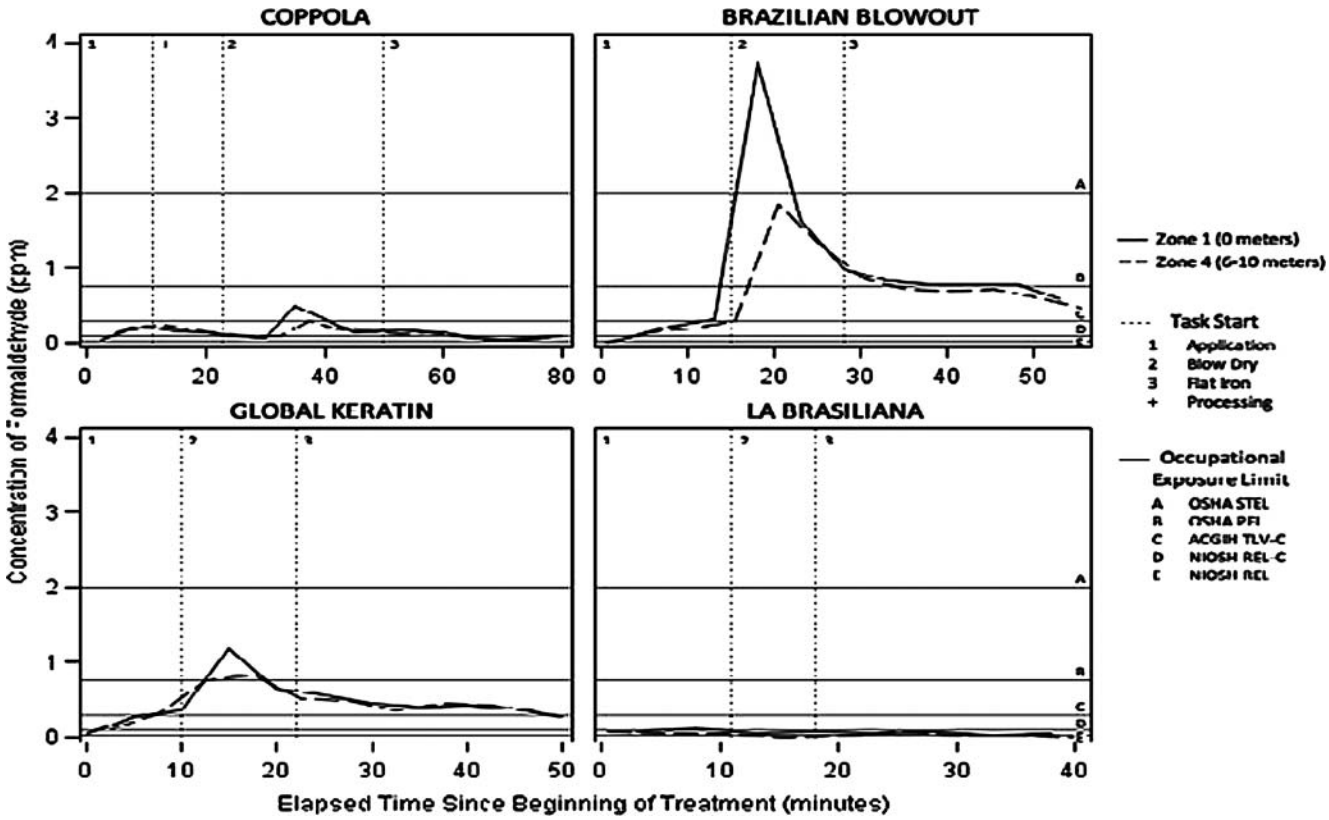

FIGURE 5. Real-time airborne formaldehyde concentrations (ppm) associated with the blow-dry and flat-iron tasks.

($p = 0.015$); similar associations were not found for cyclopentasiloxane, propylene glycol, or task durations ($p = 0.14$, 0.36, and 0.53, respectively).

DISCUSSION

Results of the bulk product analyses in this study were similar to those reported previously. Specifically, our analysis of the Brazilian Blowout product indicated the presence of formaldehyde at 11.5% (by weight), which is consistent with the findings of Oregon OSHA (6.8–11.8% in "Brazilian Blowout Acai Professional Smoothing Solution"), Health Canada (8.4%), and NIOSH (11%).[10,11,20] The Global Keratin and Coppola products also contained measurable levels of formaldehyde (average of 8.3 and 3.0%, respectively), while the La Brasiliana product contained no measurable

TABLE VII. Estimated Time-Weighted Average Concentrations of Formaldehyde (ppm)

			Estimated 8-hr TWA (ppm)[A]			
Scenario	Treatments per Day	Treatment	Zone 1	Zone 2	Zone 3	Zone 4
1	1	Coppola	0.03	0.02	0.02	0.02
	1	Brazilian Blowout	0.16	0.11	0.10	0.08
	1	Global Keratin	0.09	0.07	0.07	0.05
	1	La Brasiliana	0.02	0.02	0.02	0.02
2	4	Coppola	0.09	0.07	0.06	0.05
	4	Brazilian Blowout	0.75	0.58	0.53	0.44
	4	Global Keratin	0.39	0.31	0.30	0.25
	4	La Brasiliana	0.05	0.04	0.04	0.04
3	4	One of each of the four products tested	0.29	0.22	0.2	0.17

[A]Zone 1: 0 m, Zone 2: 0.5–1.0 m, Zone 3: 2.0–3.0 m, Zone 4: 6–10 m.

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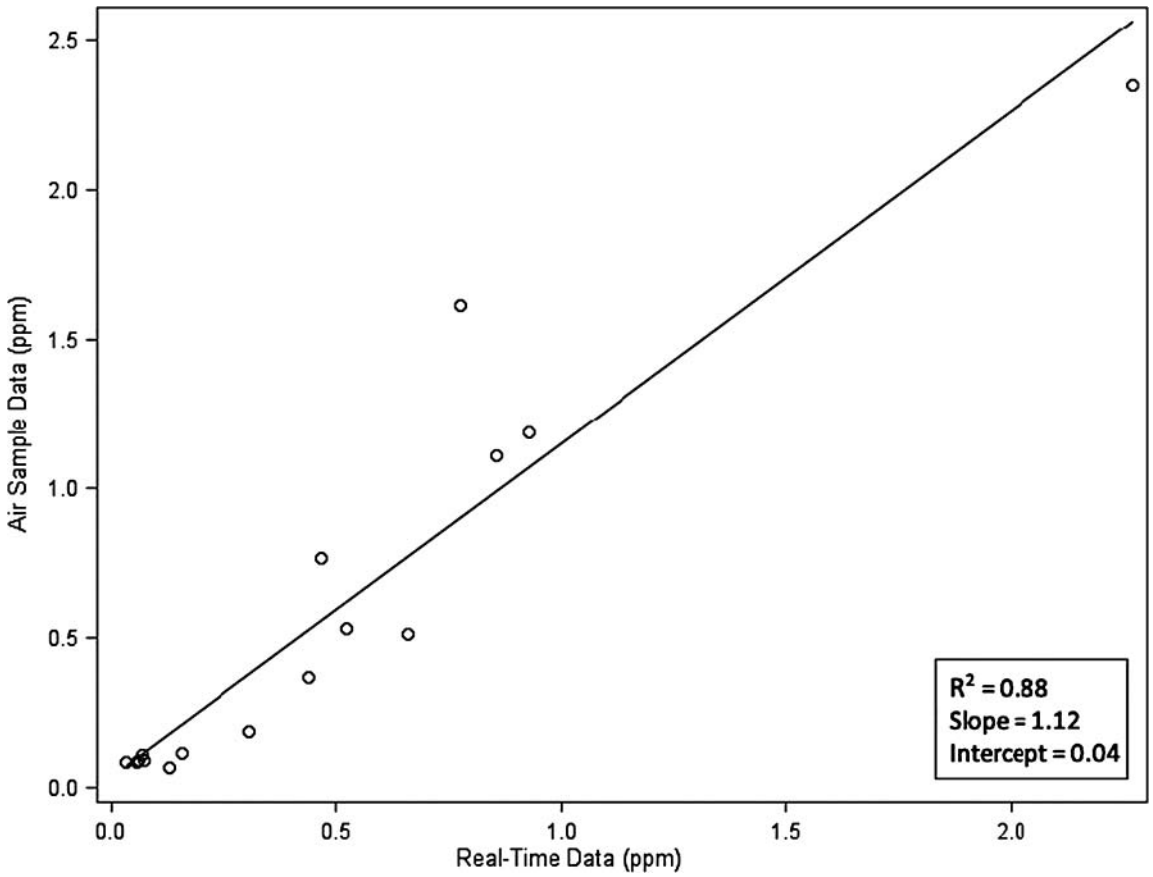

FIGURE 6. Comparison of real-time measurements with task-based active sampling results.

formaldehyde at a LOD of < 0.5 μg/mL. Bulk samples of the treatment products were also evaluated for the presence of certain glycols and siloxanes because these compounds may readily degrade to formaldehyde when heated. During hair treatment the flat iron is set to 450°F, which is well above the thermal decomposition temperature of 150 °F for siloxanes.[21] In this analysis, cyclopentasiloxane-decamethyl was detected at trace levels in La Brasiliana, and propylene glycol was detected at trace levels in Global Keratin and Coppola.[22–24] While these compounds likely contributed little to the airborne formaldehyde levels in our study, it is possible that their presence in other products (at higher concentrations) could contribute substantially.

Airborne formaldehyde concentrations measured in the hair treatment simulation study are slightly, but consistently, higher than those initially reported by NIOSH and Oregon OSHA. Specifically, mean formaldehyde concentrations reported by Oregon OSHA and NIOSH during blow-drying (0.81 and 0.84 ppm, respectively) and flat-ironing (0.47 and 0.41 ppm, respectively) with Brazilian Blowout were about one-third of the mean concentrations measured in our analysis (2.35 and 1.11 ppm). Similarly, the longer-term treatment-based and 8-hr TWAs derived from the Oregon OSHA stylist's work with Brazilian Blowout (means of 0.447 and 0.078 ppm, respectively) were roughly 50% of the values obtained in our study (means of 1.19 and 0.16 ppm, respectively). The reasons for this discrepancy are unclear, but could be because consecutive treatments were performed throughout the day in our study (as opposed to NIOSH and Oregon OSHA's "single treatment" studies), or a number of other factors, including differences in air exchange rates, room dimensions, application techniques, and so on.

Airborne levels of formaldehyde measured during the use of all four products generally followed the same concentration pattern as the products themselves: Brazilian Blowout > Global Keratin > Coppola > La Brasiliana. This pattern held true for the task-based measurements and the treatment and 8-hr TWAs, in all zones. These findings indicate that airborne levels will generally increase as the product's formaldehyde content increases. Also, airborne formaldehyde levels generally decreased with distance from the stylist. It might therefore be possible to eventually develop a predictive model that can accurately estimate airborne formaldehyde levels in different salon locations as a function of product formaldehyde content, although clearly additional data would be required, and a better understanding of the influence of air exchange rates, task duration, number of treatments per day, and other input variables would be needed.

The sampling time for the full-shift samples in this study was approximately 6 hr (371 min), thus less than a standard

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workday of 8 hr and less than OSHA's requirement of 7 hr for estimating a full-shift, 8-hr TWA.[25] For the short-term samples, the sampling duration varied from 6 to 15 min, which was due to sampling during tasks of short duration (e.g., less than 15 min with another task immediately following, such as blow-drying followed by flat-ironing). Thus, some of these concentrations may not be directly compared with 15-min OELs. However, even taking this caveat into consideration, many short-term samples likely exceeded one or more OEL.

The large disparity in the NIOSH-recommended REL of 0.016 ppm and the enforceable OSHA 8-hr PEL of 0.75 ppm introduces some uncertainty as to the characterization of our estimated 8-hour TWAs. Specifically, while the estimated 8-hr TWAs for all scenarios (in all zones) were above the NIOSH REL, they were all at or below the OSHA PEL. The NIOSH REL is within the range of background ambient levels reported in the United States and is also below the limits of detection in this study.[3] OSHA PELs in general are intended to protect "healthy workers" from long-term health effects over an extended period. They do not normally consider non-occupational receptors such as children or the elderly. It is therefore worth noting that in this study's test salon, as few as four Brazilian Blowout treatments in a single day could result in an 8-hr TWA that approaches or potentially exceeds the PEL at locations that can be considered representative of the immediate customer (Zone 1), adjacent customer (Zone 2), and even in the more remote receptionist/waiting room area (Zone 4) (Table VII). Although there are no federal standards regulating formaldehyde in indoor residential settings, other countries have set indoor exposure limits for formaldehyde, designed to protect the general population. Canada, for example, has set an indoor 1-hr limit of 0.1 ppm formaldehyde to protect against eye irritation, and an 8-hr limit of 0.04 ppm formaldehyde to protect against respiratory effects in children.[26] In short, our findings suggest that further evaluation of potential occupational and customer exposures may be warranted.

Following the 2010 Oregon OSHA investigation, a Hazard Alert was issued cautioning salon owners and stylists that the Brazilian Blowout solution contains "significant levels of formaldehyde" and also warning of potential adverse health effects, including allergic reactions, coughing, and wheezing.[27] Other states, including California, Connecticut, and Washington, have issued similar warnings. In November 2010, the Attorney General of California filed a class action lawsuit against the manufacturers of the Brazilian Blowout solution for failing to warn consumers that the product contains a carcinogen, which is a violation of California's Safe Drinking Water and Toxic Enforcement Act.

More recently, in April 2011, federal OSHA issued a Hazard Alert about potential formaldehyde exposure from using Brazilian Blowout Solution.[18] This alert provided information about health effects from formaldehyde exposure, OSHA's investigations, and how to protect salon workers.[18] Following this hazard alert, several members of Congress submitted a letter to the U.S. Food and Drug Administration (FDA) urging it to issue a voluntary recall of the product and to require proper warning labels based on results from recent testing.[28]

The current OSHA formaldehyde standard indicates that "manufacturers are required to modify their labels to indicate the presence of formaldehyde in their product," and "if the product is capable of releasing formaldehyde at levels exceeding 0.5 ppm, the label shall contain the words 'Potential Cancer Hazard'."[11] Of the products evaluated here, only one, Global Keratin, mentioned the presence of formaldehyde on its label, indicating that the formaldehyde content was < 4% (the subsequent analyses indicated that it contained 8.3% formaldehyde). Indeed, the Brazilian Blowout label specifically indicated that the product "does not contain formaldehyde." None of the labels indicated "potential cancer hazard," even though short-term measurements obtained with two of the products (Brazilian Blowout and Global Keratin) far exceeded 0.5 ppm (Table I). These findings suggest that a market survey involving analyses of hair straightening products for formaldehyde content (and an evaluation of the text of the accompanying labels) would be timely.

Strengths and Limitations

The major strength of the current study is that it addresses some significant information gaps in the previously existing data. Specifically, (1) different products with varying formaldehyde content were used; (2) personal and bystander samples were collected; and (3) samples were collected throughout consecutive treatments. The primary limitation of this study is the use of a single salon setting. The authors believe the salon chosen for this study represents a typical urban salon offering hair straightening treatments to customers, but the representativeness of this salon should be evaluated when applying these data to any other facility.

It has been suggested that the use of certain analytical methods (i.e., OSHA Method 52) may result in overprediction of formaldehyde concentrations due to the simultaneous presence of methylene glycol vapors (depending on temperature and equilibrium kinetics). However, this method was not used in our analysis.

As noted earlier, variables that should be considered when applying the data presented here to other settings include salon dimensions and air exchange rates, and the number of stylists and treatments per day. An additional limitation is that formaldehyde-spiked tubes and diffusion monitors were not provided to the laboratory for analysis as a means of quality control (to assess possible formaldehyde loss in sample handling and processing). However, if such a loss were significant, we would expect to see a trend in the correlation of the real-time data and the air sampling analytical data where the real-time data were consistently higher than the analytical results. Such a pattern was not observed (Figure 6), indicating that the impact of this loss (if any) was minimal.

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