Understanding Potential Exposure Sources of Perfluorinated Carboxylic Acids in the Workplace

MARY A. KAISER¹, BARBARA J. DAWSON²*, CATHERINE A. BARTON³ and MIGUEL A. BOTELHO¹

¹DuPont Company, Corporate Center for Analytical Sciences, Wilmington, DE, 19880, USA; ²DuPont Company, Corporate Safety, Health and Environmental Center, D6092A, 1007 Market Street, Wilmington, DE, 19898, USA; ³DuPont Company, DuPont Engineering Technology, Wilmington, DE, 19898, USA

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This paper integrates perspectives from analytical chemistry, environmental engineering, and industrial hygiene to better understand how workers may be exposed to perfluorinated carboxylic acids when handling them in the workplace in order to identify appropriate exposure controls. Due to the dramatic difference in physical properties of the protonated acid form and the anionic form, this family of chemicals provides unique industrial hygiene challenges. Workplace monitoring, experimental data, and modeling results were used to ascertain the most probable workplace exposure sources and transport mechanisms for perfluorooctanoic acid (PFOA) and its ammonium salt (APFO). PFOA is biopersistent and its measurement in the blood has been used to assess human exposure since it integrates exposure from all routes of entry. Monitoring suggests that inhalation of airborne material may be an important exposure route. Transport studies indicated that, under low pH conditions, PFOA, the undissociated (acid) species, actively partitions from water into air. In addition, solid-phase PFOA and APFO may also sublime into the air. Modeling studies determined that contributions from surface sublimation and loss from low pH aqueous solutions can be significant potential sources of workplace exposure. These findings suggest that keeping surfaces clean, preventing accumulation of material in unventilated areas, removing solids from waste trenches and sumps, and maintaining neutral pH in sumps can lower workplace exposures.

Keywords: APFO; exposure assessment; perfluoroacid; PFOA; sublimation; surface contamination; vapor pressure

INTRODUCTION

The purpose of this paper is to provide information to understand and reduce perfluorinated carboxylic acid (PFCA) workplace exposure. Even though some synthetic fluorinated compounds have existed for >50 years, their presence in occupational and environmental settings still introduces interesting challenges since in general, fluorinated compounds behave differently from hydrocarbons, the most studied class of organic chemicals. Fluorinated compounds have significantly different properties from their hydrocarbon counterparts, due in part to the extreme stability of the carbon–fluorine bond and the extreme electronegativity and small atomic radius of the fluorine atom (Banks et al., 1994). Perfluorinated compounds are hydrophobic and oleophobic. For example, on the solvatochromic II scale, an index of solvent polarity, water is 1.09, cyclohexane is 0.00, and perfluorooctane is −0.41 (Kamlet et al., 1983).

The major industrial use of PFCAs, specifically perfluorooctanoic acid (PFOA) and perfluoronanoic acid as their ammonium salts (APFO), is as an aid in the emulsion polymerization of some fluorinated monomers (e.g. tetrafluoroethylene) to manufacture some fluoropolymers (e.g. polytetrafluoroethylene).
As a process additive, the PFCA is the surfactant that enables the fluorinated monomer components to remain emulsified in order for polymerization to occur. Under some workplace conditions, its acid form, PFOA, may also be present. This paper focuses on these two chemicals, PFOA and APFO, to represent the class of PFCAs.

PFOA, measured as the anion PF$^-O$ in blood, is estimated to have a biological half-life in humans of ~2 to 4 years (Burris et al., 2002; Bartell et al., 2010). Historically, levels ranging from 0 to 100 p.p.m. have been found in the blood of workers with most of the results <20 p.p.m. (Ubel et al., 1980; Olsen et al., 1998, 2003), and these levels are significantly higher than blood levels found in the US general population averaging ~5 p.p.b. based on blood bank sampling performed in 2000–2001 (Olsen et al., 2003). The objective of this paper was to demonstrate that sublimation from surfaces and volatilization from aqueous solutions can be pathways for worker exposure to PFCAs in the workplace. Understanding these pathways will enable focus on appropriate control technologies to minimize exposure.

Because workplace monitoring has demonstrated measurable levels of organic fluorine in air (Ubel et al., 1980), we concentrated our evaluation efforts for this paper on airborne exposure. Transport studies were conducted to explore the potential for PFOA and APFO volatilization from aqueous solution and sublimation as sources of airborne emissions. Modeling was performed to determine whether volatilization and sublimation corresponded to measured air concentrations. In addition to airborne exposure, potential dermal exposure from contact with surfaces was explored qualitatively. Results from these studies were used to recommend hygiene practices to minimize worker exposure.

**METHODS**

**Air monitoring above manufacturing area sump**

Air monitoring was conducted at a facility where APFO and PFOA are currently manufactured and handled. Air samples were taken near two process sumps where pH, concentration, and water level can vary based upon operating activities. Samples were collected with the Occupational Safety and Health Administration versatile sampler with a quartz filter and XAD®-2 resin and analyzed by liquid chromatography/tandem mass spectrometry (LC/MS/MS) using procedures and analytical methods based on those described by Kaiser et al. (2005). Samples were collected at 1 l min$^{-1}$ for 8 h.

**Laboratory studies**

**Sublimation.** To determine if sublimation might be a mechanism for the material to become airborne, separate sublimation tests were conducted for PFOA and APFO. Approximately 5 g (weighed to ±0.01 mg) of the finely ground powder (PFOA or APFO) was placed in a preweighed 4 mm inside diameter borosilicate glass column (gas chromatographic inlet liner 19251-60540; Agilent, Little Falls, DE, USA). Preweighed deactivated borosilicate glass wool (Restek Corporation, Bellefonte, PA, USA) was used to contain the powder within the tube. A 1 ml min$^{-1}$ flow of filtered and dried (gas moisture trap catalog number MT120-4-D; Agilent) nitrogen was passed through the tube. A National Institute of Standards and Technology (NIST) traceable 65 mm aluminum flow meter with flow totalizer (catalog number 32044-00; Cole-Palmer, Vernon Hills, IL, USA) and a gas mass flow meter with flow controller (catalog number K-32648-04 and K-32650-70; Cole-Palmer) were used to control the flow. The glass column was placed in a gas chromatographic oven (HP series 6890; Agilent). The temperature ranged from 25 to 55°C and was held constant within ±0.4°C with the oven controls and verified by a NIST traceable thermometer (catalog number 62344-7364; VWR International, Inc., West Chester, PA, USA). The only temperature range that was covered by both the experiments was 45°C so this is the only temperature for which the data are displayed in Table 3. Mass loss at constant temperature was observed as a function of time.

**Partitioning to air from aqueous solution.** To determine if PFCAs can be released to air from an aqueous solution under various pH conditions, a solution made with 180 mg l$^{-1}$ of PFOA was placed in a 250-ml round-bottom three-necked flask. Filtered dry nitrogen was set to flow (100 ml min$^{-1}$) across the surface so that no ripples were formed on the surface. A magnetic stirring bar was used to slowly mix the liquid and minimize turbulence. The flow rate was measured (as above). The solution was buffered at pH 4.0, 5.6, and 7.0. Test chemicals and buffers are given in Table 1. Buffers were selected since, based on the pKa, we needed pHs less than neutral in order to have a range of protonated and ionized acid. The selected buffers span the range of acidic pHs reasonably anticipated to exist in process environments. The ambient temperature ranged from 23.3 to 24.7°C over the 9-day study period. Three C$_{18}$ reversed-phase extraction cartridges, connected in series with latex tubing, were placed downstream to collect the vapors from the flask headspace. Three
cartridges in series were used to ensure that all the material was collected in order to confirm that no breakthrough occurred. Cartridges were analyzed and replaced at 24-h interval (with the exception of weekends when 72-h interval was used). The cartridges were extracted with methanol and PFOA was determined via LC/MS/MS using the analytical method described by Larsen et al. (2006).

**Modeling methods**

Simple mass transfer modeling was performed to simulate volatilization from liquids and sublimation from surfaces in a manufacturing setting. Three scenarios were modeled:

1. Volatilization of PFOA from wet Sump A: containing an aqueous solution with 340 mg l⁻¹ PFOA at pH = 1.8.
2. Sublimation of PFOA from dry Sump A: with ~50% of its previously wetted surface area currently covered with dry PFOA molecules.
3. A combination of volatilization and sublimation of PFOA from Sump B: volatilization of PFOA from an aqueous solution with 54 mg l⁻¹ PFOA at pH = 6.7 and sublimation from dry walls with ~10% of their previously wetted surface area covered with dry PFOA molecules.

Input parameters were selected to represent actual facility conditions during air monitoring. Room air velocities based on manufacturing area airflow ranged from 0.0096 to 0.0143 m s⁻¹. Measured values were used for pH and PFOA concentrations. Sump surface area and water levels were based on observation of site conditions.

**Modeling partitioning to air from liquid surfaces.** Environmental Protection Agency (EPA) methods were used to estimate the mass per unit time of PFOA that would be released from a water surface. These methods use this basic relationship for describing mass transfer from an open liquid surface to air (US Environmental Protection Agency, 1994).

\[ E = KAC_L, \]  \hspace{1cm} (1)

where \( E \) = air emissions from the liquid surface, grams per second; \( K \) = mass transfer coefficient, meters per second; \( A \) = liquid surface area, square meter; and \( C_L \) = concentration of PFOA in the liquid phase, grams per cubic meter.

The mass transfer coefficient, \( K \), is estimated based on a two-phase resistance model. This model accounts for diffusion through the liquid and gas phases separately.

\[ \frac{1}{K} = \frac{1}{k_L} + \frac{1}{k_G k_{eq}}, \]  \hspace{1cm} (2)

where \( K \) = overall mass transfer coefficient, meters per second; \( k_L \) = liquid-phase mass transfer coefficient, meters per second; \( k_G \) = gas-phase mass transfer coefficient, meters per second; and \( k_{eq} \) = equilibrium partition coefficient, unitless.

Liquid-phase and gas-phase mass transfer coefficients were calculated based on EPA tools and published methods, respectively (Mackay and Matsugu, 1973; Hwang, 1982; US Environmental Protection Agency, 2007). The equilibrium partition coefficient was based on measured data and adjusted for pH and temperature conditions. Calculations and associated references for \( k_L \), \( k_G \), and \( k_{eq} \) are contained in the supplementary material (available at Annals of Occupational Hygiene online).

Estimated emissions from equation (1) were input into a simplified Well-Mixed Box Model (WMBM) equation (AIHA, 2000) to predict room concentrations of PFOA. The following simplifying assumptions were applied to the WMBM:

- Perfect mixing in the room,
- No sinks in the room,
- Constant emission rate,
- Incoming contribution of PFOA to room is zero,
- Emissions occur for \( \geq 12 \) h.

The resulting simplified equation is

\[ C = \frac{G}{Q}, \]  \hspace{1cm} (3)

where \( C \) = room concentration, grams per cubic meter; \( G \) = generation rate (calculated emission rate), grams per second; and \( Q \) = room airflow, cubic meters per second.

**Sublimation from dry surfaces.** For sublimation modeling, a dry sump surface was selected and mass transfer calculations were performed using experimentally determined solid vapor pressures. The

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**Table 1. Test chemicals and buffers**

| Chemical or buffer name | Source |
|-------------------------|--------|
| PFOA 99%                | Daikin Industries, Ltd., Osaka, Japan |
| Buffer pH 4, product code 34170-10600 | EMD Chemicals, Inc., Gibbstown, NJ, USA |
| Buffer pH 5.6–176 ml of 0.1 N sodium acetate and 24 ml of 0.1 N acetic acid | EMD Chemicals, Inc. |
| Buffer pH 7, product code 34170-115 | EMD Chemicals, Inc. |

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following basic relationship was used to describe release of PFOA into air:

$$E = KAFC_s,$$

(4)

where $E =$ air emissions from the surface, grams per second; $K =$ mass transfer coefficient, meter per second; $A =$ surface area, square meter; $F =$ fraction of surface coated (assumed 50%); and $C_s =$ concentration of PFOA at the surface, grams per cubic meter.

$C_s$ is the saturated chemical concentration at the interface between the surface and the atmosphere and is calculated from solid vapor pressure measurements, as shown in the supplementary material (available at Annals of Occupational Hygiene online). Estimated emissions were inputted into equation (3) to predict room concentrations of PFOA.

The mass transfer coefficient, $K$, was calculated using the following relationship based on boundary layer theory that assumes mass transfer in laminar flow across a flat plate.

$$K = \frac{(Sh)(Da)}{L},$$

(5)

where $Sh =$ Sherwood number, unitless; $Da =$ diffusivity of PFOA in air, square meters per second; and $L =$ length of the sump, meter.

Calculations are shown in the supplementary material (available at Annals of Occupational Hygiene online).

RESULTS

Air monitoring of PFOA/APFO manufacturing facilities

Air monitoring is routinely performed in a facility that manufactures both APFO and PFOA. During a 2-week period, monitoring was conducted near a process sump. Results showed quantifiable levels of PFOA in air (Table 2). These data suggest a correlation between increased air concentrations and decreased sump pH and water level.

Table 3. Sublimation data for APFO/PFOA at 1 ml min$^{-1}$ airflow

| APFO | PFOA |
|------|------|
| Temperature (°C) | Mass loss (mg) | Total air volume (ml) | Temperature (°C) | Mass loss (mg) | Total air volume (ml) |
| 44.8–45.6 | 0.05 | 10624 | 45.8–45.6 | 36.3 | 4407 |
| 45.5–45.8 | 0.13 | 11496 | 46.1–45.6 | 10.5 | 1576 |
| 45.3–45.8 | 0.01 | 11741 | 45.8–45.4 | 9.70 | 1421 |
| 45.1–45.8 | 0.06 | 10610 | 45.8–45.4 | 9.42 | 1378 |
| 45.1–45.9 | 0.06 | 17106 | 45.8 | 9.39 | 1427 |
| Total | 0.31 | 61577 | Total | 85.3 | 14307 |

Laboratory studies

Sublimation. Experimental results for the sublimation of APFO and PFOA at ~45°C are presented in Table 3. Both APFO and PFOA were shown to sublime in this study. The average rate of loss of PFOA was 0.36 mg h$^{-1}$, and for APFO, the average rate of loss was much lower, 302 ng h$^{-1}$ at 45°C. These data suggest that PFOA is more likely than APFO to be transported into the air via sublimation. These findings are consistent with solid vapor pressure measurements published for APFO and PFOA (AIHA, 2000; Barton et al., 2008, 2009), which show the solid vapor pressure for PFOA is approximately three orders of magnitude higher than for APFO.

Partitioning to air from aqueous solution. A graph of the mass of PFOA partitioned to air from aqueous solution as a function of time and pH is given in Fig. 1. The data suggest that the lower the pH, the more PFOA is partitioned to air from the aqueous solution, which agrees with monitoring data shown in Table 2.

Modeling studies

Modeling results for release of PFOA from wet and dry sumps are shown in Table 4. A range of measured air concentrations over time is expected due to influences of process steps and varying operator activities in the manufacturing area. Note that the degree of emissions and resulting room concentrations are correlated with the pH and concentration of the liquid in the sump.
The purpose of this work was to further understand how PFCAs behave in their various forms in order to help focus the appropriate control strategies that will minimize potential workplace exposure. Our studies showed that PFOA can actively partition into air from low pH aqueous solution and from dry surfaces. This implies that in a manufacturing setting, the source of PFOA in air could be from sumps or trenches for example, as well as material that has condensed on walls, floors, and equipment. In some cases, PFOA has been visible on surfaces in the workplace, such as sump walls. Unpublished wipe test results, using a previously published method (Botelho et al., 2009), confirm the presence of PFOA on other surfaces in process areas.

For PFOA in water, such as material present in sumps and trenches, the partitioning of PFOA from water to air is pH dependent, the lower the pH, the greater the volatilization. Assuming an acid dissociation constant (pKₐ) of 2.8 (Kissa, 1994; Burns et al., 2008), the Henderson–Hasselbalch equation (Henderson, 1908; Hasselbalch, 1916) shows that at pH 4 ~6% is in the undissociated PFOA form compared to 0.006% at pH of 7. Since PFCAs contain a very hydrophobic perfluoroalkyl-tail, the undissociated acid is much less water soluble than the perfluorooctanoate anion. In fact, the undissociated form is highly insoluble in water with a significant driving force for it to partition out of the water into the air above the water under low pH conditions. The experimental data demonstrate that a pH of 4 limits the quantity of undissociated acid leaving the surface. This understanding has direct implications in the workplace for minimizing the potential for PFCAs to become airborne. In manufacturing areas, it is common practice to wash down the work area with water into an open trench following a line break or other task in which PFOA/APFO is released from its containment. Trenches often are used to carry unwanted material from the operating area to waste treatment. These studies demonstrate that controlling the pH level in the sump to near neutral will

**DISCUSSION**

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Table 4. Measured and modeled volatilization of PFOA from sump liquid and surfaces

| Sump             | Sump conditions | Measured PFOA in air (mg m⁻³) | Modeled PFOA in air (mg m⁻³) | Comments |
|------------------|-----------------|-------------------------------|-----------------------------|----------|
| Sump A (wet)     | pH = 1.8, 340 mg l⁻¹ PFOA, liquid level = 0.13 m | Range 0.0003–0.053, 4-day average = 0.03 (n = 4) | 0.4 | Calculated emission rate from water surface 0.2 mg s⁻¹ |
| Sump A (dry)     | 50% of surface covered with molecules of PFOA, liquid level = 0 | Range 0.5–1.8, 3-day average = 1.2 (n = 3) | 0.88 | Calculated emission rate from dry sump surface 0.44 mg s⁻¹ |
| Sump B (combination of wet and dry surfaces) | pH = 6.7, 50 mg l⁻¹ PFOA, liquid level = 0.08 m, 10% of exposed walls covered with molecules of PFOA | Range 0.0082–0.0086, 2-day average = 0.008 (n = 2) | 0.0098 | Calculated emission rate from water and dry surface 0.0049 mg s⁻¹ |

*TWA = 8-h time-weighted average samples.*

![Fig. 1. Mass of PFOA transported from aqueous solution to air as a function of time and pH.](image-url)
limit the amount of PFOA that may become airborne. The lower the pH, the more undissociated PFOA is present that will be able to partition directly to the air from aqueous solution. The laboratory demonstrations showed that for water surfaces, partitioning of PFOA to air increases with decreasing pH. Air monitoring data above a sump under different pH levels has confirmed this approach to be effective in lowering airborne PFOA concentrations (see Tables 2 and 4). Table 2 data show an order of magnitude decrease in emissions over a process sump when the sump pH was adjusted from acidic to neutral conditions. As the water level in this sump decreased over time and the pH remained near neutral, emissions again increased. This increase suggests that the residual PFOA on the exposed trench surface was subject to sublimation, which was minimized when the sump level was restored. The mechanisms suggested here were confirmed through laboratory experimentation and modeling. Table 4 shows results from a different sampling campaign.

The studies demonstrated that sublimation of both PFOA, the acid, and its ammonium salt, APFO, from surfaces was a significant mechanism for airborne exposure. While volatility of the acid is understood, an explanation for volatilization of the low vapor pressure salt is warranted. The mechanism of sublimation for the ammonium salt, APFO, has been hypothesized in other work as a multistage process (Barton et al., 2009). In the first step, PFO\(^+\)H–NH\(_3\) desorbs from the solid surface as \(\text{NH}_3\)\(_\text{g}\) and \(\text{PFOH}\)\(_\text{g}\) (where \(\text{PFOH} = \text{the protonated form of perfluorooctanoic acid}\)). This dissociation likely takes place 10 000 times faster than the formation of the complex that occurred in the second step. This multistage model implies that the molecular complex PFO\(_\text{g}\) ↔ \(\text{H–NH}_3\) forms with one compound but very quickly dissociates into the gas phase as the separate species, \(\text{NH}_3\)\(_\text{g}\) and \(\text{PFOH}\)\(_\text{g}\). It also implies that when perfluorooctanoate is found in the gas phase, it may well be in the neutral acid form (PFOH or PFOA). The range in the sublimation data in Table 3 can be explained by the innate variability in the precision of the mass measurements near the limit of the analytical balance.

Modeling was effectively used to predict room concentrations of PFOA that could be released from water surfaces and/or dry surfaces in a manufacturing area. In Table 4, modeled predictions were compared with actual monitoring data taken under similar conditions. On the whole, the model reasonably predicts the relative concentration of PFOA in air over a sump. Both measured and modeled results suggest that sublimation from dry surfaces may lead to higher airborne concentrations than volatilization from aqueous solution, depending on the mass concentration on the surface. Results also suggest that aqueous solutions with low pH can contribute to higher levels of airborne PFOA than neutral pH solutions. These modeled and measured results correlate with experimental sublimation and volatilization results showing that the unique properties of PFOA and APFO may make presence on surfaces and in liquids a probable source of elevated airborne concentrations.

The laboratory and modeling studies suggest that when residual material collects on work surfaces, such as floors or trenches, and is allowed to dry, it may sublime and contribute to the airborne concentration in the workplace. For dry surfaces, transport of PFOA to air increases with increasing surface area and concentration. This understanding suggests that if a solution is spilled, the airborne concentration will be low initially and as the solvent evaporates, PFOA will sublime into the air. Therefore, immediately cleaning up spills and thoroughly washing the surface can minimize the potential airborne concentration. Also, preventing accumulation of material in unventilated areas, removing solids from waste trenches and sumps, and keeping liquid pH neutral in the trench may reduce the amount of material released into the air and should be part of an exposure control plan.

Traditional industrial hygiene practice suggests that another source of airborne exposure from surface deposition is resuspension of dust. Common factors that impact the ability of the dust to become resuspended include particle size, air velocity in the sampling area, foot traffic, temperature, and humidity. Fine particles can be easily resuspended, whereas larger particles tend to deposit. In operations with PFOA or APFO, particulate matter could consist of solid particles of APFO or other particles with PFOA on their surface. Keeping surfaces free of dust accumulation will minimize the potential for resuspension of solids.

Wipe sampling is a useful industrial hygiene tool for evaluating the effectiveness of housekeeping and decontamination programs. Unfortunately, there is not good correlation between wipe sample results and particulate airborne concentrations in the published literature (Chavalitnitikul and Levin, 1984; Caplan, 1993; ). The ability of the PFCAs to sublime makes correlation between surface and airborne concentrations even more difficult. A related paper
discusses a validated method for wipe testing on workplace surfaces (Botelho et al., 2009).

Surface characteristics of the workplace play an extremely important role in the efficiency of decontamination. The rougher and more permeable the surface, the less likely it is that the PFCAs will be efficiently removed when wiped (Botelho et al., 2009). Smooth glass and smooth stainless steel, for example, will generally allow more effective decontamination than plywood, concrete, brick, or tile. These surface characteristics also impact the ability to conduct wipe sampling and to obtain reliable reproducible results. Porous surfaces may also appear to be free of material when wipe tested after cleaning, but when wiped at a later time, may show a positive wipe from material moving out of the pores to the surface.

In addition, wipe sampling can be a tool for determining when dermal protection should be provided since dermal absorption may also be a concern from materials on surfaces. For human skin, laboratory testing has shown that the steady state APFO penetration rate is 190 ± 57 ng cm⁻² h⁻¹ after 12 h with a calculated permeability coefficient of 9.49 ± 2.86 × 10⁻⁷ cm h⁻¹. In this test, at the end of a 48-h exposure period 0.048 ± 0.01% APFO had permeated human skin (Fasano et al., 2005). No experimental data are available for PFOA. In addition to the exposure through skin permeation, when there is a possibility for skin contact (e.g. hands and lips), it is possible for the material to be ingested. Skin contact could occur from transfer of material to food or cigarettes or direct contact of the hands with the mouth.

CONCLUSIONS

Experiments and modeling show that both surface solids and low pH liquids could be sources of airborne workplace exposure to PFCAs, such as PFOA and APFO. Even when operations are not running, residual material on surfaces in the work area may result in measurable airborne concentrations. Keeping work surfaces clean can reduce the amount of material in the air and also reduce the potential for dermal absorption and subsequent ingestion. Periodically cleaning workplace surfaces including trenches and sumps so that solids do not accumulate will reduce the potential for sublimation. Neutralizing the pH level of liquids in sumps will limit the amount of PFCAs that may become airborne. Cleaning sumps will also minimize the amount of material in the liquid thus reducing the amount of undissociated material leaving the surface of the liquid and contributing to higher levels in the workplace air.

SUPPLEMENTARY MATERIAL

Supplementary material can be found at http://annhyg.oxfordjournals.org/.

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