Secondary emissions of aldehydes from consumer products in the presence of ozone

Hong Wang and Glenn C. Morrison*

Missouri University of Science & Technology, USA

*Corresponding email: gcm@mst.edu

SUMMARY
A variety of consumer products tend to coat indoor surfaces during their use and, because of their composition, consume ozone and release volatile oxidized organic compounds. Laboratory experiments were conducted to quantify the ozone reaction probability, and yields of aldehydes from the interactions of ozone with three categories of consumer products: cooking oils, personal hygiene products, and cleaning agents. Upon exposed to ozone at a range of 100~200 ppb for 3 h, ten products coating an inert surface generated secondary emissions of C_1-C_{10} aldehydes except acetaldehyde and heptanal, with nonanal as the most prominent compound. Cleaners and cooking oils emitted aldehydes with summed yields ranging from 0.1 to 0.6. All personal hygiene products except soap exhibited low aldehyde yields. Unsaturated fatty acid esters, such as oleic, linoleic, and linolenic esters, common constituents in oils and soaps, are likely responsible for relatively high secondary emission rates of aldehydes in residences.

KEYWORDS
Consumer products, Ozone, Secondary emission rates, Aldehydes, Surface reactions

INTRODUCTION
Consumer use of cooking oils, cleaning agents, air fresheners, and personal hygiene products tend to leave ozone-reactive residues on indoor surfaces and on the user. Oils, cleaning agents, soaps and other personal hygiene products, can contain unsaturated fatty acids and their esters as well as terpenes and terpenoids as scenting agents or active solvents. Ozone reactions with triglycerides, fatty acids and related compounds tend to generate aldehydes and carboxylic acids (Razumovskii et al., 1984). Morrison and Nazaroff (2002) suggested that biogenic oils coated on carpets during manufacturing process were responsible for these “secondary emissions” of aldehydes from carpets. These unsaturated compounds react rapidly with ozone (Weschler, 2000), to generate potentially harmful secondary pollutants (Weschler, 2006). Ozone reactions with terpenoids produce formaldehyde, acetone, glycolaldehyde, formic acid, hydrogen peroxide, hydroxyl radicals, and secondary organic aerosols (Destaillats et al., 2006; Weschler and Shields, 1999). The products of ozone/terpene reactions cause upper air way and eye irritation (Weschler, 2006; Wolkoff et al., 2000).

Wang and Morrison (2006) reported that in field homes secondary pollutants are also generated by reactions between ozone and the low-volatility compounds that coat surfaces from activities such as cooking and cleaning. Various surfaces (e.g. carpet or kitchen countertop) contribute in very different ways to secondary emissions indoors. Secondary emissions from carpets diminish as ozone depletes manufacturing oils originally present on newly installed carpets. However, surfaces such as countertops are repeatedly coated with reactive consumer products. Over time, countertops and other frequently coated or cleaned surfaces may become the dominant contributor of secondary aldehydes to indoor air.
While there have been several studies of ozone reactions with cleaners containing volatile and semi-volatile terpenoid compounds (Singer et al., 2006), little is known about secondary emissions from the products that contain other unsaturated constituents (e.g., unsaturated fatty acid esters) and that are likely to remain on surfaces indefinitely, or until removed intentionally by cleaning. The goal of this research is to quantify ozone reaction probability and the secondary aldehyde yield from consumer products that coat indoor surfaces during normal use. These two parameters are system independent and can be used to extrapolate ozone uptake rates and secondary emission rates to systems under a variety of mass-transfer conditions and differing ozone concentrations. These parameters are quantified by measuring ozone consumption rates and aldehyde emission rates from coatings exposed to ozone in a laboratory reactor.

**METHODS**

**Consumer products.** We selected three categories of products in this study: cooking oils; personal hygiene products; and cleaning agents. These products were selected using the following criteria. (1) likely to contain unsaturated fatty acid esters such as cooking oils and soap. (2) widely used personal hygiene products, such as shampoo and lotion. (3) cleaning agents that are used over large surface areas such as wood furniture or floor cleaner and kitchen countertop cleaner. The most popular brands of products were identified by consulting the purchasing manager of a large grocery and sundries store in Rolla, MO, USA. Information on the selected products is shown in Table 1.

**Coating methods.** An inert polycarbonate sheet, which was shown to be unreactive with ozone by laboratory experiment, was used as the substrate and coated with various consumer products individually. The transparent polycarbonate sheet was cut into a 23 cm-diameter circular shape to fit into the stainless steel reaction chamber. Before being coated, the polycarbonate sheet was cleaned with methanol and rinsed with distilled water. A 1 cm-wide teflon circular mask covered the edge of the sheet, while coating, to ensure that the coating area was consistent. By coating within the ring, we also prevented the substrate from contaminating the chamber surfaces during installation. Consumer products were coated on polycarbonate sheet to mimic coating on a counter or floor. The following coating methods were followed:

1. **Bar soap.** A bar of bath soap was rubbed with tap water-wetted cellulosic lab tissues. And then the tissues were used to spread soap uniformly within the teflon ring on the polycarbonate surface. For one experiment, the soap-coated surface was tested directly. In another experiment, the soap-coated surface was evaluated after being rinsed with tap water and then wiped with the clean tissues.

2. **Liquid soap, body wash, and shampoo.** The products were dispensed onto the surface and wiped uniformly within the ring on the surface with the tap water-wetted tissues.

3. **Hand lotion, oil soap (wood furniture cleaner), and unused canola oil.** The products were dispensed on the polycarbonate surface, and then wiped uniformly within the Teflon ring on the surface with tissues.

4. **Counter cleaner and furniture polish.** The products were sprayed directly within the Teflon ring on the surface and wiped uniformly with tissues.

5. **Spray canola oil.** The canola oil was sprayed on a piece of paper held perpendicular to the polycarbonate surface (as a consumer might spray a pan before cooking), allowing excess spray droplets to settle naturally on the polycarbonate surface.

6. **Frying residue.** Canola oil was studied to investigate how cooking and dispersal on nearby surfaces may influence ozone uptake and secondary emissions. The polycarbonate substrate along with five microscope slides were placed 5 cm away from...
a frying pan where 5 g of canola oil was used to fry a small fish. The polycarbonate sheet and microscope slides remained there during cooking process which lasted for around 20 min. In the process of cooking, vaporized canola oil, and probably also oils and other materials from the fish, deposited on the surface. Five microscope slides were used to determine surface coating coverage area.

Table 1. Summary information for ten products.

<table>
<thead>
<tr>
<th>Product</th>
<th>Brand</th>
<th>Composition[a] [package]</th>
</tr>
</thead>
<tbody>
<tr>
<td>canola oil</td>
<td>Great value</td>
<td>Triglycerides (capped bottle)</td>
</tr>
<tr>
<td>canola oil</td>
<td>Great value</td>
<td>triglycerides (canola oil), soylecithin, water, propellant [trigger spray]</td>
</tr>
<tr>
<td>liquid soap</td>
<td>Equate</td>
<td>water, sodium laurate sulfate, sodium lauryl sulfate, fragrance [pump dispenser]</td>
</tr>
<tr>
<td>bar soap</td>
<td>Irish spring</td>
<td>soap (sodium tallowate, sodium cocoate, and/or sodium palm kernelate), water, hydrogenated tallow acid, fragrance [bar]</td>
</tr>
<tr>
<td>body wash</td>
<td>Equate</td>
<td>water, sodium laurate sulfate, cocamidopropyl betaine, fragrance [pump dispenser]</td>
</tr>
<tr>
<td>shampoo</td>
<td>Suave</td>
<td>water, ammonium lauryl sulfate, ammonium chloride, cocamide MEA, fragrance [capped bottle]</td>
</tr>
<tr>
<td>hand lotion</td>
<td>Vaseline</td>
<td>water, glycerin, stearic acid, mineral oil, glycol stearate, orange oil, lavender oil [pump dispenser]</td>
</tr>
<tr>
<td>counter cleaner (soap)</td>
<td>Great value</td>
<td>surfactant [trigger spray] fatty acids and terpenoids [capped bottle]</td>
</tr>
<tr>
<td>wood floor cleaner (oil)</td>
<td>Murphy</td>
<td>fatty acids and terpenoids [trigger spray]</td>
</tr>
</tbody>
</table>

[a] Major compositions of consumer products are listed. Components of interest in this research, and that are likely to react readily with ozone, are listed in **bold**.

**Surface coating coverage area analysis.** The polycarbonate surface was coated with products in two ways: uniform coating and non-uniform coating. For uniform coating, such as soap, the coating coverage area was the $346 \text{ cm}^2$ area within the Teflon ring. For non-uniform coating, such as the coatings of spray oil or oil from frying, the coating coverage area was the total area covered with deposited oil droplets. The non-uniform coating areas were indirectly measured by imaging the surface coverage with a camera (MD 130 electronic eyepiece) attached to a microscope. The average coating coverage areas for spray oil and frying residue were $46.0 \pm 1.4$ and $4.7 \pm 2.1 \text{ cm}^2$ respectively. We used Bright-Line counting chambers and the microscope to determine the average diameters of spray oil droplets and frying residue oil droplets, which were $0.19 \pm 0.05 \text{ mm}$ and $0.03 \pm 0.007 \text{ mm}$ respectively.

**Secondary emission rate experiments.** Secondary emissions of aldehydes formed by reactions between ozone and consumer products were measured using the apparatus shown in Figure 1. The experiments were conducted using a 10-L electropolished stainless steel chamber with an inner diameter of 24 cm. The chamber is sealed with a platinum cured silicone gasket and a lid attached to the chamber body with three spring clips. The lid was equipped with 0.32 cm (1/8 inch) and 0.63 (1/4 inch) stainless steel fittings (Swagelock®) for inflow and outflow, respectively. The circular polycarbonate sheet was placed on the bottom of the chamber with the coating side up. The system consisted of an ozone generator, humidifier, emission chamber, sampling system, and an ultraviolet photometric ozone analyzer (Teledyne model 400A). The relative humidity and inlet ozone mixing ratios were controlled at 50±5% and 150–250 ppb respectively by adjusting flow rate passing through three air streams in the system. Reaction products were collected from an outlet port. A mass flow meter was used at the exhaust stream pre-experiment to examine if there was any leak in the system. High molecular weight aldehydes (C_5–C_{10}) were collected on sorbent tubes.
containing Tenax-TA. Light molecular weight aldehydes (C₃-C₄) were captured using cartridges (Supelco) filled with silica gel coated with dinitrophenylhydrazine (DNPH) that also incorporated an ozone trap.

Laboratory experiments were conducted to show that SERs reach steady state conditions 1.5 hours after initiating ozone exposure in the chamber (Wang and Morrison, 2006). Therefore, to be certain of steady-state conditions in the experiments, we exposed the surface to ozone for 3 hours before collecting aldehyde samples. Aldehyde emissions were measured before and during exposure to ozone. Experimental procedures are the same as those described in Wang and Morrison (2006) except that 1 h exposure samples were not collected. Chemical analyses are described in Wang and Morrison (2006).

**Reaction probability.** The surface reaction probability, $\gamma$, is defined as the rate that ozone is irreversibly consumed by a surface divided by the rate of ozone-surface collisions. The reaction probability is given by

$$\gamma = \frac{\langle v \rangle}{4 \left( \frac{1}{v_d} - \frac{1}{v_t} \right)}$$

where $v_d$ is the deposition velocity for the specific surface, $v_t$ the transport limited deposition velocity for the same surface, $\langle v \rangle$ is the Boltzmann velocity for the pollutant, which for ozone is $3.62 \times 10^4$ cm s⁻¹ at 296 K (Cano-Ruiz et al., 1993). The deposition velocities are derived from inlet and outlet ozone concentrations for the surface of interest ($v_d$) and for a perfect sink ($v_t$) (Wang and Morrison, 2006).

Figure 1. Experimental apparatus for measuring ozone-induced secondary emission rates from products.

**RESULTS**

**Yields.** The yield, defined as the ratio of the molar emission rate of an analyte to the molar loss rate of ozone to that surface, is used to characterize product formation. Figure 2 shows yields for the identified oxidation products from all coatings. The nonanal yield ranged from 0 for body wash and shampoo to 0.32 for oil soap. For products used mostly in kitchens, including soaps, counter cleaners, and oils, the average nonanal yield was 0.22, indicating that
22% of ozone consumed at the surface produced nonanal. This value is similar to the average nonanal yield of 0.24 for kitchen countertops evaluated in five houses (Wang and Morrison, 2006). This correspondence supports the hypothesis that nonanal emitted from the kitchen countertops is a result of the reactions between ozone and soaps, counter cleaners, and oils. The summed aldehyde yield ranged from 0 to 0.60, which is comparable to the yield range (0.02 to 0.53), observed for five indoor surfaces in field homes (Wang and Morrison, 2008). However, the summed aldehyde yields in this study exhibited a wider range than the overall yield for the identified products observed in simulated aircraft during 4-hour flights (0.25 to 0.30) (Weschler et al., 2007). The narrower product yields observed in the aircraft experiments were derived, in large part, from reactions of ozone and skin oils coating passengers, their clothing, and other cabin materials. The wider yield range in our study is due to the wide varieties of “pure” products tested in this research, including some products not likely to be encountered in aircraft. In our study, personal hygiene products generated aldehydes with low summed yields (0 to 0.22), whereas, cleaning agents generated aldehydes with higher summed yields (0.26 to 0.60).

**Reaction probabilities.** The reaction probability, also known as the uptake coefficient, acts as an indicator of the surface reactivity. The reaction probabilities with uncertainties for each product are shown in Figure 3.

![Figure 2. Ozone-induced aldehyde yields for all coatings.](image)

Uncertainties were derived from error propagation analysis of Eq 1 and duplicate experiments for each product. Surfaces coated with all consumer products had a wide range of reaction probabilities, spanning an order of magnitude from $2.0 \times 10^{-6}$ to $9.7 \times 10^{-5}$. The reaction probabilities observed in this study fall within the range of $1.9 \times 10^{-6}$ to $1 \times 10^{-4}$ for five indoor surfaces, living room carpet, bedroom carpet, living room wall, kitchen floor, and kitchen countertop, in five homes measured in three seasons (Wang and Morrison, 2008). The soaps, cleaning agents, and some cooking oils had reaction probabilities of approximately $10^{-5}$, the same order of magnitude as those of kitchen countertops reported by Wang and Morrison (Wang and Morrison, 2008). Thus, these agents may be responsible for ozone uptake at these surfaces. All personal hygiene products except soap exhibited low reaction probabilities, of the order of $10^{-6}$. The low reaction probabilities of personal hygiene products, mostly used in bathrooms, could be related to the fact that bathroom counter surface exhibited very low reactivity with ozone in field homes. Wang and Morrison (2008) studied the bathroom counter in field homes in one season; they observed, but did not report in that paper,
that the SERs of all targeted aldehydes from the bathroom counters were less than the method detection limits. Unused canola oil had the highest reaction probability among all products. The reaction probability for unused canola oil ($9.7 \times 10^{-5}$) is lower than the reactive uptake probability of ozone by liquid oleic acid and linoleic acid, which are $(8.3 \pm 0.2) \times 10^{-4}$ and $(1.2 \pm 0.2) \times 10^{-3}$ respectively (Moise and Rudich, 2002). Canola oil is composed of saturated fatty acids, such as palmitic and stearic acids, and unsaturated acids, such as oleic, linoleic and linolenic acids. Unsaturated fatty acids are responsible for secondary emissions in the presence of ozone. Although fatty acid compositions in canola oil vary among different manufacturers, generally oleic and linoleic acid comprise less than 80% of the fatty acid composition of canola oils. As a result, the overall reaction probability of canola oil is anticipated to be lower than those for pure oleic or linoleic acid.

**DISCUSSION**

For products composed of the same proportion of fatty acid esters, we would anticipate the same secondary emission patterns. Furthermore, the ratio of individual aldehyde yields should be consistent with the proportion of fatty acid esters compositions in products.

![Log scale reaction probabilities for all coatings.](image)

Morrison and Howard (2000) performed laboratory chamber experiments to investigate interactions of ozone with a surface coated with linseed oil. They showed that the mass emission fraction of 3, 6-nonadienal, 3-nonenal, and nonanal obtained in experiments were nearly identical to the predicted emission fractions based on the proportion of linolenic, linoleic, and oleic acid present in linseed oil. In this research, we observed different yield patterns among unused, frying residue, and spray canola oil. The yields of propanal, hexanal, and nonanal from spray canola oil had a ratio of 16%, 17%, and 67% respectively in the total aldehyde yield, which are close to the proportions of linolenic, linoleic, oleic and erucic esters in canola oils. Unused canola oil emitted much less hexanal and propanal than expected but vegetable oil compositions can vary widely. For frying residue, hexanal accounted for 50% of the total molar SER. Fish is high in omega-3 fatty acids, which is primarily composed of α-linolenic acid. Upon exposure to ozone, α-linolenic acid is expected to generate 3, 6-nonadienal, 3-hexenal, and propanal. In the process of cooking, double bonds might have shifted and resulted in high yield of hexanal. The large proportion of hexanal yield from frying residue might be due to transformations during cooking or contamination from α-linolenic acid associated with fish.
CONCLUSIONS
Our experimental results demonstrate that a variety of consumer products react with ozone to produce aldehydes. Cleaning agents such as oil soap and furniture polish are used to promote hygiene, aesthetics and material preservation. However, cleaning, cooking and other activities will be accompanied by irritating, odorous, or even carcinogenic (e.g. formaldehyde) pollutants. As long as these products are used indoors, the volatile organic compounds generated from ozone-initiated surface chemistry will persist. Yet it is impractical to remove many of these kinds of products from indoor environments. Indeed, our skin oils are also responsible for much reactivity in some settings (Weschler et al. 2007). Instead, reducing indoor levels of ozone may be far more practical and bring the further benefit of reduced exposure to ozone itself.

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REFERENCES