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Setting maximum emission rates from ozone emitting consumer appliances in the United States and Canada

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ABSTRACT

A Monte Carlo analysis of indoor ozone levels in four cities was applied to provide guidance to regulatory agencies on setting maximum ozone emission rates from consumer appliances. Measured distributions of air exchange rates, ozone decay rates and outdoor ozone levels at monitoring stations were combined with a steady-state indoor air quality model resulting in emission rate distributions (mg h^{-1}) as a function of % of building hours protected from exceeding a target maximum indoor concentration of 20 ppb. Whole-year, summer and winter results for Elizabeth, NJ, Houston, TX, Windsor, ON, and Los Angeles, CA exhibited strong regional differences, primarily due to differences in air exchange rates. Infiltration of ambient ozone at higher average air exchange rates significantly reduces allowable emission rates, even though air exchange also dilutes emissions from appliances. For Houston, TX and Windsor, ON, which have lower average residential air exchange rates, emission rates ranged from −1.1 to 2.3 mg h^{-1} for scenarios that protect 80% or more of building hours from experiencing ozone concentrations greater than 20 ppb in summer. For Los Angeles, CA and Elizabeth, NJ, with higher air exchange rates, only negative emission rates were allowable to provide the same level of protection. For the 80th percentile residence, we estimate that an 8-h average limit concentration of 20 ppb would be exceeded, even in the absence of an indoor ozone source, 40 or more days per year in any of the cities analyzed. The negative emission rates emerging from the analysis suggest that only a zero-emission rate standard is prudent for Los Angeles, Elizabeth, NJ and other regions with higher summertime air exchange rates. For regions such as Houston with lower summertime air exchange rates, the higher emission rates would likely increase occupant exposure to the undesirable products of ozone reactions, thus reinforcing the need for zero-emission rate standard.

1. Introduction

The presence of ozone in the indoor environment has serious health consequences in addition to detrimental effects on building and household materials. Human exposure to ozone has been found to cause a variety of adverse health effects including decreases in pulmonary function and increases in reported symptoms such as headache, eye irritation, and cough (USEPA, 2006). In epidemiological studies, ozone concentrations below the National Ambient Air Quality Standard have been associated with wheezing and difficulty breathing among infants, particularly those whose mothers have physician-diagnosed asthma (Triche et al., 2006). Both short-term (Bell et al., 2006) and long-term (Jerrett et al., 2009) exposure to increased ozone concentrations have also been linked to premature mortality with incremental increases of as little as 10 ppb. Toxicological studies with human subjects have indicated a no observable adverse effect level (NOAEL) of 40 ppb (Adams, 2002).

Concentrations of ozone in the indoor environment vary as a function of outdoor contributions and indoor sources. Indoor/outdoor ratios that result from outdoor ozone contributions alone range from <0.05 in tightly sealed buildings (or those utilizing charcoal filters), to 0.85 in buildings with very high air exchange rates. Excluding extremes, the I/O ratio is more often in the range of 0.2–0.7 (Weschler, 2000). Copiers, laser printers, electronic air cleaners and ozone generators can act as a source of indoor ozone with emission rates ranging from 0.1 to 100 mg h^{-1} (Britigan et al., 2006; Jakober and Phillips, 2008; Mason et al., 2000; Mullen et al., 2005; Phillips and Jakober, 2006; Waring et al., 2008). This range is comparable to outdoor air as a source of ozone which can rise to ~100 mg h^{-1} for a residence on a highly polluted day.

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Indoor sources of ozone have become a concern for the indirect effects of ozone chemistry as well as the direct effect of exposing occupants to more ozone. Ozone reactions with terpenoids released by cleaners (Nazaroff and Weschler, 2004), air fresheners and personal care products (Corsi et al., 2007) generate respiratory irritants (Anderson et al., 2007; Rohr et al., 2002; Wolkoff et al., 2000) and low-volatility species that condense to substantially increase sub-micron sized aerosol mass concentrations (Hubbard et al., 2005; Rohr et al., 2003; Waring et al., 2008; Weschler and Shields, 1999). Ozone reactions with indoor surfaces such as carpet (Morrison and Nazaroff, 2002), painted walls (Reiss et al., 1995) and soiled surfaces (Wang and Morrison, 2006) generate volatile aldehydes, carboxylic acids and ketones. In certain settings, much of the indoor ozone conversion rates are due to reactions with skin oils that coat humans, their clothing and other surfaces (Coleman et al., 2008; Weschler et al., 2007). Reactions taking place on (Pandrangi and Morrison, 2008; Wisthaler and Weschler, 2010) or near the body (Corsi et al., 2007) increase product and aerosol concentrations in the breathing zone (Rim et al., 2009), relative to the rest of the building space. Use of ozone emitting appliances increases the indoor concentrations of all of these reaction products. Even air "purification" systems designed to remove particles by electrostatic precipitation, which generate ozone as a byproduct, have been shown to *increase* aerosol concentrations when used in the presence of terpenes (Waring et al., 2008) from consumer products such as air fresheners. The adverse impacts of ozone and its chemistry may affect a significant fraction of the U.S. population: in a survey of California homes, 10% of respondents owned devices that intentionally or unintentionally emitted ozone (Piazza et al., 2007).

Because of the prevalence and the observed and inferred effects of using ozone emitting appliances in buildings, agencies have targeted these for regulation. The Food and Drug Administration (FDA) standard (21CFR801.415) has designated a 50 ppb maximum level of ozone that is generated by or that results in an accumulation from ozone generating devices used in enclosed spaces intended to be occupied by people for extended periods of time. In a review for the US Consumer Product Safety Commission (CPSC), Shaughnessy et al. (2006) concluded that human toxicological studies did not support a limit lower than 50 ppb, in large part because few of these studies exposed humans to levels below this value. The current limit prescribed by the FDA does not discriminate between ozone contributed from an air cleaner as compared to that originating from outdoor infiltration of ozone from both anthropogenic and non-anthropogenic sources. The FDA limit applies to the total accumulation of ozone in the space which ultimately must account for contributions from both the air cleaner and those from outdoor air. The California Air Resources Board (ARB) adopted a regulation (ARB, 2007) to limit the ozone emitted from indoor air cleaning devices. The new regulation bans air cleaning devices that do not meet UL Standard 867 which limits the "ozone emission concentration" to 50 ppb. The California regulation is written such that, based on the contribution from the air cleaner alone, the indoor concentration may not exceed 50 ppb in a typical room. This regulation explicitly excludes contributions from outdoor or other background ozone. Although UL Standard 867 includes conservative assumptions to reduce the likelihood of indoor environments exceeding 50 ppb, a cleaner that meets the standard can raise indoor mixing ratios above 50 ppb because the background is non-zero. In addition Health Canada is seeking input on a proposed indoor air quality guideline for ozone. In this case, they propose to set the limit at 20 ppb for an 8 h averaging period (Lloyd, 2009), but do not necessarily exclude the contribution from outdoor ozone. This value was chosen as a compromise between the reference concentration of 4 ppb, which is 10% of the NOAEL derived from human studies (Adams, 2002), and what is anticipated to be achievable in homes based on measurements in Canadian homes (Liu et al., 1995). In each of these regulatory examples, an explicit concentration value is applied to set limits on devices, because "concentration" can be directly connected to health outcomes by way of exposure or intake.

Ozone concentrations resulting from the use of the same device in two different buildings will most certainly be different. Indoor air concentrations are dynamic, changing substantially over a day's time and are influenced by variables such as penetration rates of outdoor ozone through the building shell, air exchange rate, filtration, chemistry, building size and surface area. Because of these issues, a more comprehensive method for evaluating devices would be to place a ceiling on the source emission rate of ozone, S, that provides adequate protection for most situations.

The source emission rate has a direct and predictable impact on indoor concentrations. For assessing the influence of one variable over another, or for assessing the impact of a control strategy, the mass-balance model proves useful for assessing indoor microenvironments (Nazaroff and Cass, 1986). This model has been successfully applied to simple and very complex systems (Carslaw, 2007). Typically, the mass-balance model is applied to a single well-mixed compartment such as a room or whole residence. Applying a time-averaged (Riley et al., 2002) mass-balance model to ozone in a single well-mixed compartment, the source emission rate, S, can be shown to be

$$S = (\lambda + k_d)VC_L - V\lambda C_o P \quad (1)$$

where λ is the air exchange rate (h^{-1}), V is the room or building volume, C_L is the maximum indoor ozone limit concentration goal (e.g. 20 ppb or 40 $\mu g\ m^{-3}$), C_o is the outdoor ozone concentration and P is the penetration of ozone through the building shell (i.e. 1 = 100% penetration). Variable parameters (λ, k_d, C_o) are time-averaged values and are assumed to be uncorrelated. The net ozone decay rate, k_d, combines ozone losses due to air chemistry, deposition to surfaces, attenuation in recirculation or ventilation systems, and any other first order loss mechanisms. The air exchange rate is assumed to be entirely due to infiltration of outdoor air into the compartment and excludes room-to-room air exchange.

Thus, if all independent parameters are known, a maximum source emission rate for an ozone generating device, S, can be defined by specifying a maximum indoor ozone concentration, C_L. Direct use of Equation (1) to specify a maximum emission rate using "typical" parameters is of marginal value for regulatory purposes because building characteristics and outdoor ozone concentrations are extremely heterogeneous. Parameter values can range over orders of magnitude depending on the choice of building. Also, choosing variables by a qualitative metric (such as, "to be protective"), may not directly provide clear guidance on *how* protective such a choice is. To overcome these limitations, we apply a Monte Carlo analysis to account for the natural distribution of values for λ, k_d, and C_o. The resulting distribution will be directly related to a quantitative measure of protection. Because of the recent regulatory interest in consumer-oriented products, this study focuses on residences. The specific objective of this research is to develop distributions for source emission rates that can be used by a regulatory agency to help answer the question: What emission rate, S, protects a specified fraction of residence-hours from experiencing an ozone concentration higher than a specified limit, such as 20 ppb, while indoors?

2. Methods

2.1. Monte Carlo analysis

Monte Carlo analysis provides for the calculation of a probability distribution for an unknown parameter, S in this case, if it can