Health Canada Santé Canada

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NATIONAL AMBIENT AIR QUALITY OBJECTIVES FOR GROUND-LEVEL OZONE

SCIENCE ASSESSMENT DOCUMENT

A Report by
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on Air Quality Objectives
and Guidelines

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Part 3 of 7

6 ASSESSMENT OF EXPOSURE

This chapter discusses factors which influence human exposure to ozone and presents information on the relationships between ambient, indoor and personal[1] ozone levels. Estimates of the frequency of contact between the Canadian population and ozone through air were extrapolated from the results of modelling efforts for three urban areas in Canada. This assessment does not consider human exposure to ozone that occurs after ozone has transferred to another environmental medium (i.e. deposition into food, water or soil) because ozone's high reactivity makes exposure via another route unlikely.

6.1 CONCEPTS

Just as several factors influence outdoor ozone concentrations—photochemical production, long-range transport of non-locally produced ozone, intrusion from the stratosphere, and removal by scavenging—several factors influence individual exposure to ozone. *Exposure* is defined as any contact at a boundary (surface) between a target (who is being exposed) and a specific contaminant concentration for a specified time interval (National Research Council (NRC), 1991). For airborne contaminants, the boundary consists of the outer (skin) or inner (respiratory tract epithelium) surface of the body (Sexton & Ryan, 1988). The *dose* is defined as the measured or estimated exposure at the inner contact surface; that is, the actual amount of pollutant that enters the body and reaches the target tissue, in this case the respiratory system (Sexton & Ryan, 1988). In determining the likelihood of human health impacts, scientists require clarity when estimating dose and/or exposure, since the concentrations measured at the outer boundary may not equal those that reach the inner boundary. This assessment, therefore, focuses on the key extrinsic determinants of a response: magnitude (concentration), duration (length of time) and pattern of exposure, and the ventilation rate of the individual at the time of exposure (Hazucha, 1987; Silverman et al., 1976; United States Environmental Protection Agency (U.S. EPA), 1978, 1986, 1993).

The NO_X/VOC Management Plan states that "in summer months, more than half of all Canadians are routinely exposed to ambient air ozone concentrations that are known to cause adverse effects on health" (p. xii, Canadian Council of Ministers of the Environment (CCME), 1990). Although this statement includes an estimate of the size of the exposed population, it does not include observations or estimates of who is exposed, where, when or how often. Therefore, to determine the likelihood of human health impacts of ground-level ozone in Canada, scientists and policy-makers require better estimates of human exposure to ozone.

There are two ways of determining exposure: *directly* at the point at which it occurs—by providing each person with a personal monitor to carry for the period of the study; or it can also be *predicted*—using concentration, fate and distribution information combined with data (from time activity diaries and questionnaires) on activities which bring the individual in contact with the contaminant.

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[1] This is the ozone concentration experienced by an individual during normal daily acitivities.

6.2 DIRECT EXPOSURE ASSESSMENT

6.2.1 Personal Monitoring

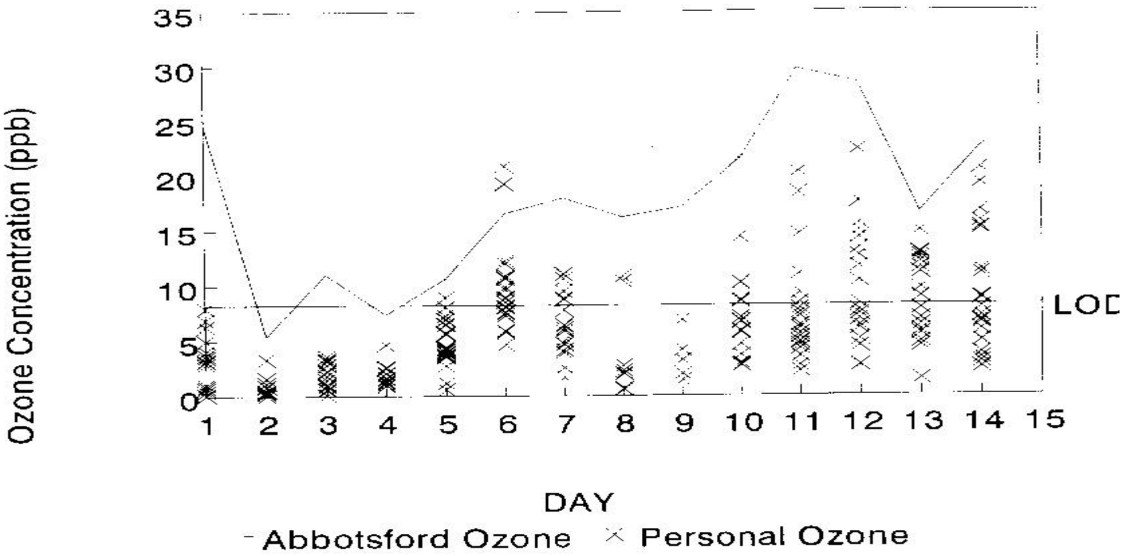
Brauer and Brook (1995) demonstrated the effects of time-activity patterns on personal ozone exposure during studies in the Lower Fraser Valley (LFV) during the summers of 1992 and 1993. They collected 14 days of personal samples (24-hour average) in the summer of 1992 from two groups of individuals: 25 Health Unit workers (Group 1) and 25 individuals from a Lutheran overnight camp (Group 2). Each participant recorded where they were (indoors, outdoors, in transit and in what location) for each hour of the day. In the summer of 1993, 15 adult farmworkers (Group 3) wore passive samplers during the work shift (6-14 hours) for 25 days. From Groups 1,2 and 3 respectively, the researchers collected 304, 287, and 219 valid personal ozone samples.

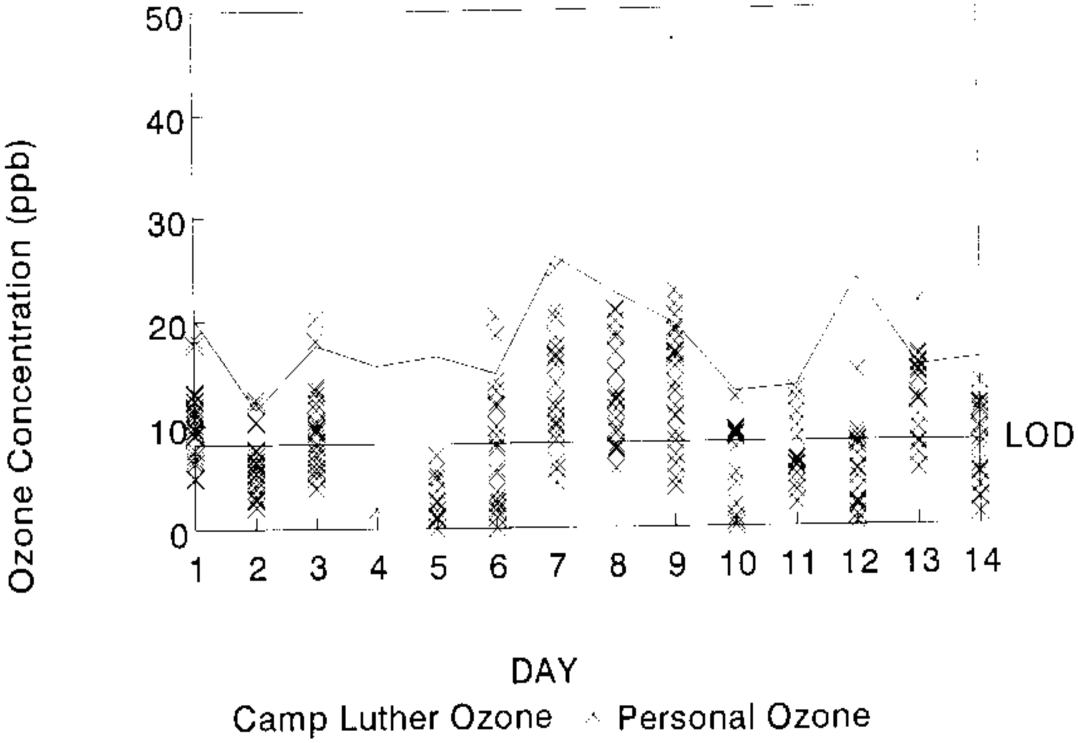
In addition, Brauer and Brook co-located passive samplers with continuous ozone analyzers at three fixed ambient monitor (FAM) sites: Pitt Meadows (Airport), Abbotsford in 1992, and Surrey in 1993. They also collected daily 24-hour passive samples (n=115) for 35 days. After calculating the passive monitor sampling rate, they compared the 24-hour average ozone concentrations from the passive sampler with the mean of the hourly average concentrations from the FAM. They found a good agreement between the samplers (r^2=0.75) as defined by the linear relationship: passive [O_3] =0.95 × continuous [O_3]. The authors then used the monitor closest to the area where the subjects were during the daytime period to compare between personal and FAM ozone concentrations.

Figure 6.1, showing the relationship between the FAM and personal ozone samples for Groups 1 and 2, reveals that personal exposures were quite variable and substantially lower than fixed site concentrations. The mean personal exposures did follow the same temporal trend as the FAM data. The mean ratios of 24-hour personal to fixed site concentrations were 0.35 (Group 1) and 0.53 (Group 2). Brauer and Brook hypothesized that the differences in personal-to-fixed ambient measurement ratios were due to the relative amount of time spent outdoors: Group 1 spent less time outdoors (9%) than did Group 2 (25.8%). The personal exposures from Group 3 were quite variable. While some measurements were below the FAM concentrations, a significant number ware above it. The mean ratio of personal-to-FAM concentrations for Group 3 was 0.96, due to the fact that the participants spent the entire sampling period outdoors. An examination of duplicate personal ozone samples revealed substantial variability in measured exposures (35%). The authors concluded that the difference was due to random variability rather than true differences in personal exposure.

Liu et al., (1993) assessed ozone exposures in State College, Pennsylvania in the summer of 1991. Twenty-three children aged 10 - 11 years participated, each wearing a passive sampler for 12 hours during the daytime. Participants recorded their time-activity, which was subsequently aggregated into four groups: home, near home, school, and other. Six 12-hour indoor daytime, five 12-hour indoor night-time, four 24-hour outdoor, and one 12-hour daytime outdoor samples were collected at each home. Ambient concentrations were measured at a FAM site, along with 12-hour daytime and night-time passive samples.

Figure 6.1 Relationship Between Fixed Location (daily mean ozone concentrations) and Personal Exposure Samples for Group 1 (top) and Group 2 (bottom) Study Populations





The analysis revealed a significant correlation between the collocated passive samplers and the FAM; the Pearson's correlation coefficient was 0.95 ($p<0.01$). Twenty-four-hour outdoor concentrations measured at the FAM significantly correlated with concentrations measured outside the homes ($r=0.81$, $p<0.01$). Despite this high correlation, however, the mean concentrations at the FAM site (37.8±10.7 ppb) were significantly higher than the mean concentrations at outdoor home sites (29.8±14.3 ppb). The mean ratio of outdoor home concentrations to 24-hour FAM was 0.80±0.25. Liu et al. (1993) found differences in the ratio of outdoor to FAM 24-hour ozone levels when they grouped the homes into regions. They attributed the differences in spatial variability to population density, housing density, traffic density and the proximity of NO sources.

Twelve-hour daytime indoor concentrations exhibited a diurnal pattern, with daytime concentrations greater than nighttime concentrations (Liu et al., 1993). The results showed a significant correlation between indoor and outdoor home concentrations ($r=0.56$, $p<0.01$), suggesting that indoor levels are due to penetration of ozone indoors. The grand mean ratio of daytime indoor/outdoor (I/O) ratios was 0.45±0.23 (range 0.07-1.16). Significant differences in the mean I/O ratios by home were attributed to differences in air flow, with ratios increasing with elevated air flow.

Daytime personal exposures correlated with daytime indoor ($r=0.55$, $p<0.01$) and outdoor levels at home ($r=0.41$, $p<0.01$) and at the FAM ($r=0.36$, $p<0.01$) (Liu et al., 1993). Mean ratios of daytime personal concentrations to daytime indoor, outdoor and FAM site concentrations were 1.69 ± 3.03 (range 0.02-26.10), 0.59 ± 0.52 (range 0.01-3.44), and 0.44 ± 0.29 (range 0.01-1.35) respectively. In other words, on average personal exposures were higher than indoor concentrations, and lower than outdoor concentrations outside the home and measured at the FAM site.

A similar methodology was followed during the first phase of the Canadian Research on Exposure Assessment Modelling (CREAM) study, which measured exposures to residents in Toronto in the winter (January to March) and summer (June to August) of 1992 (Liu et al., 1995). Monitoring was conducted in 40 homes each season in the Greater Toronto Area. In the winter, indoor, outdoor and personal samples were measured weekly over three consecutive weeks; in the summer, 12-hour daytime and nighttime samples were measured for five consecutive days. Personal 12-hour daytime measurements were taken the same days. Each participant filled out a time-activity diary. Passive samplers were co-located with a FAM at a downtown site, measuring weekly ozone concentrations in the winter and 24-hour concentrations in the summer.

Tables 6.1 and 6.2 present the descriptive statistics for personal, indoor, outdoor and FAM measurements for the winter and summer (Liu et al., 1995). Wintertime personal ozone concentrations were similar to indoor concentrations, while outdoor concentrations were greater. Concentrations measured outside the home were greater during the daytime than during the nighttime. Indoor concentrations were similar for both daytime and nighttime (Table 6.2), except in the two homes with malfunctioning electrostatic air cleaners. Personal concentrations were on average similar to indoor concentrations and lower than outdoor concentrations in both seasons. The ratio of summer 12-hour daytime personal to calculated 12-hour daytime FAM concentrations averaged 0.45 (range 0-1.32).

Table 6.1 Ozone Levels During the Winter in Toronto (7 Day Average)

Sample	N	Mean	S.D.	Max	95%	90%	75%	50%	25%	Min
outdoors-home	72	15.4	6.0	31.4	23.8	23.8	18.9	13.7	11.2	0.4
indoors-home	114	1.6	4.1	29.4	4.0	2.3	1.3	0.7	0.3	0
indoors-work	38	0.7	0.7	3.1	2.8	1.4	1.0	0.5	0.2	0
personal	71	1.3	2.9	19.6	2.9	2.1	1.5	0.6	0	0
FAM	8	9.3	4.2	17.3	17.3	17.3	12.1	9.2	5.1	4.7

Table 6.2 Ozone Levels During the Summer in Toronto (12-Hour Average)

Sample	N	Mean	S.D.	Max	95%	90%	75%	50%	25%	Min
outdoors-home, day	199	19.1	10.8	54.7	42.3	33.5	24.4	19.0	11.4	0
outdoors-home, night	160	9.4	10.2	77.8	26.6	19.4	13.1	6.1	3.9	0
indoors-home, day	199	7.1	12.6	149	22.6	15.7	11.8	4.3	0	0
indoors-home, night	160	6.2	9.5	66.1	22.4	15.8	8.9	2.7	0	0
workplace, day	93	10.0	11.6	69.4	27.8	22.2	14.3	6.9	0	0
personal, day	424	8.2	8.7	52.9	25.9	19.6	11.0	6.2	2.2	0
FAM, day	12	18.4	12.6	40	40	37	28.5	16.5	9	0
FAM, 24-hour	51	15.5	9.2	47	35	26	20	14	9	1

The outdoor concentrations exhibited spatial variability between the homes and the FAM site measurements, even though the winter weekly and summer daytime measurements correlated with the FAM measurements (r=0.98 & 0.79, respectively). Concentrations were lower in the downtown area FAM sites, likely because of a higher density of NO sources and surface areas available for scavenging ozone. Liu et al. (1995) did not examine the impact of this variability on personal exposure because of insufficient time-activity information.

6.2.2 Personal Monitoring Data as Predictors of Population Exposures

Personal monitoring studies conducted in Canada and in the US have demonstrated that mean personal exposures to ozone are highly correlated with the data from FAM, suggesting that ozone data from FAM used in epidemiological studies can adequately represent population exposure.

The results of the personal monitoring studies indicate that individual exposures are quite variable, measuring lower and occasionally higher than indoor or ambient monitors. Personal exposure ranged from 0 to greater than 100% of ambient concentrations. It would be unrealistic, though, to estimate population exposures using ratios of personal to outdoor concentrations from these few studies, because the sample sizes were small and the selection of participants was not random enough to allow for generalizations to the population as a whole. However, based upon the average personal exposure measurements being less than 100% of FAM concentrations, it is reasonable to infer that population exposures will be lower than ambient concentrations, being significantly diluted by time spent indoors. Other researchers (Hayes, 1989; Weschler et al., 1992) have shown that exposure is typically dominated by ozone that has penetrated indoors from the ambient environment.

6.3 PREDICTIVE EXPOSURE ASSESSMENT

Rather than infer exposure solely from readings of ambient monitors, exposure models bridge the gap between fixed ambient monitoring data and personal exposures. The general model mathematically represents exposure as $c_m x\ t_m$ (NRC, 1991), where a person spends time t, in microenvironment m, having a time-averaged pollutant concentration c. Each person's exposure is computed by summing the time-weighted microenvironmental concentrations experienced by that person's visiting various microenvironments (Duan, 1982; Fugas, 1975; Sexton & Ryan 1988).

Ambient monitoring data provide the basis for estimates of ozone concentrations in different locations because ozone has no significant indoor sources (the primary source is ambient penetration). Modifiers are applied to the ambient concentration according to local influences; for example, multiplying the ambient concentration by an I/O ratio is a common approach to estimating indoor levels.

6.3.1 Microenvironmental Concentrations of Ozone

The ability to estimate ozone levels in various outdoor and indoor locations is key to characterizing individual exposure. Indoor levels of ozone are usually less than ambient concentrations. The formation, transport and destruction of ozone indoors are influenced by indoor sources (ozone generators operating to remove smells or freshen air), outside air infiltration, indoor air circulation rates, and indoor surface composition (furniture, walls, rugs, etc.). Several researchers have reported that ozone deposits onto indoor surfaces at significant rates (Reiss et al., 1994, Weschler et al., 1991).

Measurements made in various microenvironments during the summer of 1992 (Liu et al., 1995) provided mean concentrations ranging from 0 ppb (reception area) to 19 ppb (clean room). Maximum indoor concentrations ranged from 0 ppb to 72 ppb. The authors reported that the I/O ratios of ozone for both the winter (0.07±0.10) and summer (0.40±0.29) varied markedly in both seasons, with winter much lower than in summer ($p<0.05$). During summer The 12-hour daytime I/O ratio averaged 0.30±0.32 while the nighttime ratio was 0.43±0.54 (difference not significant, $p=0.45$).

The literature reports a wide range and high variability in I/O ratios (Zhang & Lioy, 1994). Indoor ozone has been measured in office buildings, museums, hospitals, residences and inside motor vehicles (McKee, 1994; Weschler et al., 1989). Most I/O ratios are in the 0.5 to 0.8 range, and I/O in residences do not appear to be different from public buildings. Weschler et al. (1989) measured simultaneous indoor and outdoor concentrations in an office-laboratory complex and reported that indoor concentrations closely track the outdoor concentrations with a diurnal pattern. However, indoor ozone concentrations measured in Houston (McCurdy, 1994) showed low and flat levels (i.e. did not display peaks). A re-evaluation of the Houston data by Johnson (cited in McCurdy, 1994) revealed statistically significant differences in indoor concentrations depending upon the use of air conditioners. Because air exchange (Ach) rates are quite low in air-conditioned buildings, how closely indoor concentrations track outdoor concentrations depends upon the tightness of the building envelope (Ach rates) and the ambient ozone levels. Indoor/outdoor ratios are high for indoor microenvironments with high Ach rates, and high ambient ozone levels; they are smaller when ambient ozone is low, due to more efficient ozone scavenging.

Liu et al. (1995) showed that wintertime I/O ratios increased significantly in homes with electrostatic air cleaners. The weekly I/O ratios averaged 0.13 ± 0.12, up from 0.07 ± 0.10. Liu et al. also showed that I/O ratios for motor vehicles are greater with the windows open (0.68 ± 0.18) than with the windows closed (0.25 ± 0.33). Johnson et al., (1995) reported median values for the vehicle I/O ratios ranging from 0.07 to 0.41, depending upon the conditions. Several of the sites monitored by Weschler et al. (1989) had office equipment that could generate ozone. At those sites, ozone concentrations indoors remained low during work hours.

6.3.2 Time-Activity Patterns

Estimates of exposure to ozone can be calculated with varying degrees of specificity, depending upon the development of exposure scenarios and the selection of values for exposure parameters (exposure frequency and duration, time-activity patterns, inhalation rate and microenvironmental ozone concentration). Commonly used default values for inhalation rate mask the inherent variability in population inhalation rates, which depend upon such factors as sex, age, weight and physical condition, as well as activity level (U.S. EPA, 1989). Standard default values for time-activity patterns are also used because of the lack of adequate activity pattern data. Population exposure estimates often do not deal with individuals who spend greater or lesser amounts of time in different microenvironments that correspond to different levels of exposure. Because ozone is primarily an outdoor contaminant, high-end exposures will occur when people are outdoors engaged in recreation or employment activities. For example, athletes and children are considered at risk to the effects of ozone because they spend time outdoors engaged in physical activity, thereby increasing both their duration of exposure and their ventilation rate. The increase in ventilation slightly increases the dose to the terminal bronchiolar region, and significantly increases the pulmonary regional total dose and the dose in the proximal alveolar region (Bates, 1994).

6.3.3 Population Exposure Estimates

Population exposure models provide an aggregate estimate of exposure for a large number of persons by combining individual exposure estimates to generate a distribution of exposures. The models simulate the movement of each person, in a specified population group, through a series of microenvironments, with each person exposed to routinely measured ambient concentrations adjusted for that microenvironment.

The probabilistic National (Ambient Air Quality Standard) Exposure Model (pNEM) provides estimates of the distribution of ozone exposures within a defined population for a specified exposure period. The exposure estimates presented here are for the general population, not a population subgroup, based upon three years of ambient air quality data. Unless otherwise specified, the results are from Johnson et al. 1994 and Zhang, 1996.

Below is a brief summary of the exposure model followed by the ozone estimates for each of the three cities. See Johnson et al. (1995) for a more detailed description of pNEM.

Overview of pNEM Methodology

The pNEM methodology consists of the following steps:

1. Define a study area, a population of interest, appropriate subdivisions of the study area, and the exposure period to be investigated.
2. Define demographic groups and microenvironments and construct a corresponding activity database.
3. Divide the population of interest into an exhaustive set of cohorts.
4. Develop an exposure event sequence for each cohort for the exposure period.
5. Estimate the pollutant concentration, ventilation rate, and physiological indicators (if applicable) associated with each exposure event.
6. Extrapolate the cohort exposures to the population of interest and to sensitive subgroups of interest.

The exposure analysis is limited to three urban areas, Montréal, Toronto and Vancouver. The areas were selected because a large percentage of the Canadian population live in and around these urban areas; each city has the minimum number of ambient monitors (three) required for pNEM. Within each city, the study area is defined as an aggregation of exposure districts. Information on the distribution of air quality data around each ambient monitor, as well as population and commuting data at the census tract level was not available. In this application of pNEM, exposure districts were constructed according to 1991 census subdivisions and linked to a FAM located in or near the subdivision. pNEM assumed that the ambient ozone concentrations throughout each exposure district could be estimated from, and represented by, data at the FAM. The number of districts for each urban area varied from seven to nine based upon the number of FAMs having valid air quality data in the study area. Monitors not considered representative of population exposure (e.g., at top of the CN Tower) were not included. The exposure period was defined as the ozone season (May 1 to September 30) within each calendar year for three years (1988-1991).

The population of interest in the exposure analysis was 5,228,455 people, 25% of the total urban population within these three cities. Each person living and working in one of the defined exposure districts was assigned to only one cohort to provide a means of linking exposure to ambient ozone levels. The model assumed that each cohort contained persons with identical exposures during the specified exposure period. Cohorts were defined by specifying home district, work district, and demographic group (defined by age, sex and working status), and residential air conditioning (AC) system. The inclusion of AC systems accounted for differences in indoor levels due to penetration of ambient ozone indoors. Identifying demographic groups according to age and working status accounted for potential differences in activity levels, which influenced the likelihood of experiencing health effects.

The cohort-specific time-activity data were provided by the Cincinnati Activity Diary study (CADS) data, collected in 1985 (Johnson, 1987). Information on both the microenvironment and the breathing rate [variable denoting slow (sleeping), slow (awake), medium or fast] associated with each activity was organized by study subject and 24-hour (midnight to midnight) time period. The diary records for one subject for a 24-hour period were designated as a ‘person-day’. Each person-day is indexed by the following factors: season (summer or not summer), demographic group, temperature (cool or warm) and day type (weekday or weekend).

Justification for using the CADS database to represent the activity patterns of Canadians was provided by an analysis by Hobden (1994) which included:

- the Cincinnati study produced one of the best exposure-related time-activity databases;
- Cincinnati had a similar climatology as major Canadian cities; and
- the population of Cincinnati and surrounding area was roughly similar in size to the larger Canadian cities.

It is possible that differences in metropolitan characteristics—such as interurban distances, city lay-out and geography, route designs, public transit systems—and environmental characteristics—such as climate and latitude—all have the potential to influence how a given population uses its time. Given the uncertainties in time-activity data, and the lack of validation of many activity studies at the time of this analysis, the CADS database was the largest time-activity database available that explicitly included all of the data inputs required by the pNEM modelling methodology.

In constructing the activity data base, a computerized sampling algorithm randomly drew activity diary records relating to individual 24-hour periods from a pool of person-days which matched the cohort with respect to demographic group, and which matched the calendar day by season, day type, and temperature classification. Because CADS diary data were only available for a few days, the algorithm randomly selected data day by day from multiple subjects for the whole exposure period. This provided a better representation of the variability of exposure that was expected to occur among the persons included in each cohort.

To estimate exposures for a particular cohort, the algorithm matched the demographic characteristics of the population under study, together with the season, temperature classification and day type, with the existing categories in the activity data base for each day in the pollution season, to construct an exposure event sequence (EES). Each EES was a series of events with durations from 1 to 60 minutes at a particular combination of geographic area and microenvironment for each hour of each day for each cohort. The EES was used to determine a corresponding sequence of exposures, event-by-event.

Each exposure was defined by an ozone concentration and a ventilation rate indicator. Ozone concentration during each exposure event was assumed to be a function of the microenvironment and exposure district associated with the event. A continuous sequence of hourly average ozone concentration was developed for each combination of microenvironment and district. The microenvironment was one of:

- indoors - residence with central AC system
- indoors - residence with window AC units
- indoors - residence with no AC system
- indoors - nonresident locations
- outdoors - near road
- outdoors - other
- in vehicle

A mass-balance algorithm, described in detail in Johnson et al. (1994), generated the hourly average indoor ozone concentration during hour *h,* as a function of the indoor ozone concentrations at the end of the preceding hour (*h*-1), the ozone concentration outdoors during hour *h*, the air exchange rate during hour *h*, and an ozone decay factor. pNEM assumed that there were no indoor sources of ozone and that the concentration in a particular microenvironment was constant during a particular clock hour. Concentrations in the two ambient microenvironments (i.e. outdoors) were treated identically. This is likely to over-estimate ozone concentrations near the road because it does not account for potential ozone scavenging by nitric oxides emitted from motor vehicles.

Values for the air exchange rate and the ozone decay factor were sampled from distributions on a daily basis where appropriate (Table 6.3). Point-estimates were assumed for the parameters lacking representative databases. The opening and closing of windows in the residential microenvironments was simulated by an algorithm which specified a window status (open or closed) for each clock hour. The hourly assignments were made according to the cohorts air conditioning system (central, window units, none), the average temperature of the day, and the window status during the previous clock hour. The probabilities used in pNEM were developed from the CADS data.

Table 6.3 Exposure Parameter Values of Distributions & Point-estimates

Exposure Parameter	Microenvironment	Value
Ozone decay factor (ppb/hr)	indoors - residential and nonresidential locations	normal distribution, arith. mean=4.04; std. dev.=1.35 min=1.44; max=8.09
	in vehicle	72.0
Air exchange rate (Ach) (m^3/hr)	residence - windows closed	Lognormal distribution, geo mean = 0.53, geo. std. dev.=1.704, lower bound=0.063, upper bound = 4.47
	residence - windows open	Point estimate=6.4

	nonresidential building	Lognormal distribution, geo. mean = 1.285, geo. std. dev.=1.891, lower bound=0.19, upper bound=8.69
	vehicle	Point estimate=36

pNEM/O_3 also estimated the equivalent ventilation rate (EVR), defined as ventilation rate divided by body surface area, for each exposure event. The product of EVR and ozone concentration was defined as the dose delivered during the event. For a given age category (child or adult) and breathing rate, the algorithm simulated EVR values for each exposure event by randomly sampling from a truncated lognormal distribution. EVR values were not permitted to exceed an upper limit (EVRLIM), which varied with demographic group and event duration. The algorithm for determining EVRLIM used estimates of VO_{2max} (volume of oxygen uptake by the body), maximal and submaximal ratios of ventilation rate to oxygen uptake rate, and body surface area specific to the demographic groups associated with the cohort.

Estimates of ozone concentration, EVR, and the multiplication of ozone concentration by EVR (i.e. delivered dose) were developed for each exposure event and combined to produce time-weighted estimates for each clock hour for each cohort. The resulting year-long sequence of hourly cohort-specific estimates of exposure were extrapolated to the general population of each city by weighting according to the estimated population size of each cohort. This involves estimating the number of persons in each exposure district by demographic group, and estimating the fraction of homes falling into the three air conditioning categories. The populations of the commuting cohorts were developed from census data specific to each exposure district. In this fashion, the number of persons at risk (the sum of the estimated population size for all cohorts) was obtained for each study area.

Results of the pNEM Analyses

The following tables summarize exposure estimates for five runs of the model for the total population (including all cohorts, regardless of demographic group) within each of the three study areas for each of the three years. Multiple runs are required because pNEM is a probabilistic model. The multiple runs create a stable result based upon the empirical or theoretical probabilistic distributions of some variables. The following tables show the percentage of each study area population that was estimated to experience one or more one-hour daily maximum exposures above 82 ppb (current Canadian Ambient Air Quality Objective for 1-hour maximum ozone) (Table 6.4); the estimates for one-hour daily maximum exposures above 50 ppb (Table 6.5); the results for six-hour daily exposures above 50 ppb (Table 6.6) and the corresponding eight-hour daily exposure above 50 ppb (Table 6.7).

Table 6.4 Percentage (Standard Deviation) of the Total Study Area Population Experiencing One or More One-hour Daily Maximum Ozone Exposures Above 82 ppb.

Study Area (Population)	1988	1990	1991
Toronto (2597702)	99.39 (0.55)	82.82 (2.67)	92.05 (1.85)
Montréal (1462640)	91.86 (6.92)	30.51 (5.87)	64.44 (7.53)
Vancouver (1168113)	65.45 (2.84)	55.89 (8.01)	3.49 (2.28)

The following general statements apply to the results presented in Table 6.4. Of the nine combinations of city and year:

1. Toronto-1988 has the highest percentage of people experiencing one-hour or more, ozone exposures above 82 ppb (99.39%).
2. Vancouver-1991 has the lowest percentage of people experiencing one-hour or more, exposures above 82 ppb (3.49%) as well as the lowest percentage of people in 1988 (65.45%).
3. Montréal has the lowest percentage of people experiencing one-hour or more, exposures above 82 ppb in 1990 (30.51%).
4. Based on a three-year average for each city, the cities can be ranked from highest to lowest exposure as Toronto (91.42%), Montréal (62.27%) and Vancouver (41.61%).

Table 6.5 Percentage (Standard Deviation) of the Total Study Area Population Experiencing One Or More One-hour Daily Maximum Ozone Exposures Above 50 ppb.

Study Area (Population)	1988	1990	1991
Toronto (2,597,702)	100 (0)	100 (0)	100 (0)
Montréal (1,462,640)	100 (0)	99.24 (0.29)	99.72 (0.11)
Vancouver (1,168,113)	95.23 (1.20)	95.50 (1.23)	86.03 (2.06)

The following statements apply to the one-hour daily maximum estimates presented in Table 6.5. Of the nine combinations of city and year:

1. Toronto has the highest percentage of people experiencing one-hour daily maximum ozone exposures above 50 ppb (100%) for each of the three years. In 1988, Montréal also had 100% of the population experiencing one-hour daily maximum exposures above 50 ppb.
2. Vancouver has the lowest percentage of people experiencing one-hour daily maximum exposures above 50 ppb in each of the three years: 86.03% in 1991, 95.23% in 1988 and 95.50% in 1990.
3. Based on the three-year averages for each city, the ranking from highest to lowest exposure remains Toronto (100%), Montréal (99.65%) and Vancouver (92.25%).

Table 6.6 Percentage (Standard Deviation) of the Total Study Area Population Experiencing One Or More Six-hour Daily Maximum Ozone Exposures Above 50 ppb.

Study Area (Population)	1988	1990	1991
Toronto (2,597702)	99.97 (0.06)	98.65 (0.56)	99.74 (0.13)
Montréal (1,462,640)	97.66 (1.30)	42.05 (13.06)	98.10 (0.40)
Vancouver (1,168,113)	77.79 (0.89)	81.12 (2.92)	20.61 (6.44)

Table 6.7 Percentage (Standard deviation) of the Total Study Area Population Experiencing One or More Eight-hour Daily Maximum Ozone Exposure above 50 ppb.

Study Area (Population)	1988	1990	1991
Toronto (2,597,702)	99.63 (0.45)	94.24 (2.95)	97.49 (10.8)
Montréal (1,462,640)	95.07 (0.81)	69.00 (6.18)	95.39 (2.90)
Vancouver (1,168,113)	69.43 (2.27)	64.89 (4.18)	7.60 (4.81)

A few key features of the multi-hour exposure results of all nine combinations of city and year presented in Tables 6.6 and 6.7 follow:

1. Toronto-1988 has the highest average percentage of individuals experiencing six- and eight-hour daily maximum ozone exposures above 50 ppb (99.97% and 99.63%, respectively).
2. Vancouver-1991 has the lowest average percentage of individuals experiencing six- and eight-hour daily maximum ozone exposures above 50 ppb (20.61% and 7.60%, respectively).
3. Based on a three-year average of six- and eight-hour exposures for each city, the cities can be ranked from highest to lowest exposure as Toronto, Montréal and Vancouver.

Comparing the three-year average one-hour maximal exposures with the multi-hour exposures, as expected, more people were exposed to one-hour maximal ozone above 50 ppb than to other exposure parameters. More people were exposed to eight-hour above 50 ppb than one-hour above 82 ppb.

Limitations of the pNEM/O_3 Methodology

There is considerable uncertainty in using the modelled exposure estimates to calculate health impacts, just as there is uncertainty in extrapolating the results of pNEM to other urban areas. pNEM generates just one stochastic path as its output. Because estimates of person-days are computed from that path, estimates vary from run to run. Although McCurdy (1993) showed that an infinite number of pNEM runs are not required to produce a distribution thought to be similar to the population exposure distribution, it is desirable to be able to quantify the uncertainty in the exposure estimates. Exposures estimated from pNEM/O_3 need to be compared with those measured from a small group of individuals in demographic groups suspected to be at risk for health effects from ozone exposure.

Model distributions are dependent on the detail of information available to characterize each input parameter. Time-activity patterns are affected by land use, traffic patterns, public transit systems, recreational opportunities and environmental characteristics. Most time-activity databases have not been validated. The existing data comes from too limited an area base to make valid national estimates of population exposures. For example, outdoor workers and children are currently under-represented in the human activity data base. Exposure modelling requires a larger file of human activity patterns that better reflects the amount of time that true outdoor workers (i.e., those individuals who work outdoors at least six hours/day, on average) and children spend outside daily. Additional analysis is also required on the potential differences in time-activity between Canadians and Americans.

The season-long exposure event sequence is constructed from the data from multiple subjects and may not adequately account for the day-to day repetition of activities common to individuals.

The application of pNEM to a particular combination of city and year produces a series of cohort-specific exposure sequences. Tabulating the person-hour estimates by demographic group and time of day produces a distribution of ozone concentrations for the person-hours associated with the indicated clock hour and demographic group (i.e., a diurnal pattern of exposure). Reviewing these data indicate that exposure distributions may vary significantly from group to group when clock hour is held constant. In addition, the likelihood of exposures above a certain cutpoint can be identified by clock hour. This work has not been presented here, although it is available for the three cities.

pNEM/O_3 tends to underestimate the number of people who experience multiple occurrences of high exposure while engaged in activities. There is uncertainty around the EVR estimates used in pNEM because of the small sample sizes in the studies from which the data was obtained. Finally, there is further uncertainty in the ozone level in some indoor microenvironments because the data for air exchange rates and ozone decay rates are rather limited.

6.4 'AMBIENT' EXPOSURES COMPARED TO PREDICTED EXPOSURES

Levels of ozone measured at fixed ambient monitors (FAM) were historically, and continue to be, used as surrogates for human exposure. Ozone is measured continuously, throughout the year, at FAMs located according to land use (i.e. urban, suburban, rural and remote). Most of the Canadian population (76.6%) lives within urban areas. Urban sites exhibit two daily ozone concentration maxima, occurring mid-afternoon and during the early morning. Night-time ozone concentrations at most urban sites often attain close to 0 ppb due to ozone scavenging by NO_x emitted from cars and local industry. Urban sites experience frequent episodic, elevated concentrations of ozone, and maximum concentrations occur during the summertime (May to September).

Table 6.8 illustrates the differences in the mean ozone concentrations and frequency with which the daily maximum ambient concentrations exceed one-hour maximum of 82 ppb (current Canadian Ambient Air Quality Objective) in several areas. There is considerable year-to-year variability in the number of days with ozone concentrations above a specified concentration at individual stations. For example, in extreme years (1988) the days greater than 82 ppb are two to three times higher than the period average shown in Table 6.8.

Table 6.8 Mean Ozone Concentrations (Standard Deviation) and Average Days per Year with Ozone (1-hour) > 82 ppb (1986-1993)

Region/Site	1-hr max. ozone (ppb) (1995 and 1996)	8-hr average ozone (ppb) (1980-1992)	Average Days with Ozone >82 ppb per year (1986-1993)
Southern Atlantic	-	-	3
Montréal	35.6 (6.4), n=8	26.5 (2.4), n=6	4
Rural Québec	-	-	2
Toronto	47.3 (9.1), n=9	28.5 (1.2), n=3	15
Southern Ontario	-	-	18
Prairies	-	-	1
Vancouver-LFV	31.2 (4.1), n=12	25.8 (3.2), n=9	2

Comparing ambient ozone data with the data from pNEM (Tables 6.4-6.7) reveal that the two data sets are coherent. Toronto, that had the highest ambient ozone concentrations compared with Montreal and Vancouver, also had highest amount of predicted population exposures. A significant proportion of the total study population is exposed to daily maximum average concentrations > 82 ppb. Therefore assuming the fixed site monitoring data are representative of human exposure, more than 50% of Canadians are potentially exposed to ozone levels that cause adverse health effects, although that exposure, on average, is relatively infrequent. The pNEM data are in line with Canadian hospitalization studies (see Chapter 12.3) that have consistently shown a lower hospitalization risk associated with ozone in Vancouver and Montreal than in other parts of the country.

6.5 CONCLUSIONS

Exposure assessment involves estimating the intensity, frequency, and duration of human contact with ozone. Ozone levels vary from year to year depending on the meterological conditions; hot, sunny summers usually produce higher ozone levels than do cool, rainy summers. Individual and population-estimated exposure also varies from year to year. Exposure is defined as any contact at a boundary between a person and a specific ozone concentration for a specified time interval.

Direct personal monitoring studies measure the concentration of ozone in the immediate microenvironment (breathing zone) of the person. Results from these studies indicate that personal exposures follow a similar temporal pattern to that from FAM monitoring. This supports that FAM data are representative of population exposure. Personal exposures can be higher but are usually lower than FAM data. Generally, outdoor measurements overestimate personal exposures by greater than 50%. The studies have reported wide variability in individual personal exposures, and have demonstrated that the amount of time people spend in a given location significantly influences exposure. This second point is supported by other human exposure field studies (conducted over the years) indicating that time-activity patterns are the most important determinant of a person's exposure (Ott, 1989).

The personal monitoring data were collected over relatively long averaging times. Because ozone builds and declines gradually over the course of the day in urban and non-urban areas, varying degrees of individual exposure are associated with the hourly concentrations. The 12-

hour, 24-hour, and weekly averaging exposures collected using the passive sampler cannot assess hourly exposures, even though shorter times (such as 1-hour maximum) are considered more relevant for the health effects. Short-term ozone concentrations within a community vary much more rapidly in time and space than do long-term average concentrations. Personal monitoring data have not been very useful in predicting population exposures due to small sample sizes and unrandom selection of participants in those studies.

Monitoring the concentration of ozone in various microenvironments, integrating the data with the time spent in each, and summing the time-weighted microenvironmental concentrations over a specified time period produce an indirect estimate of exposure. Simple models have been developed (Brauer & Brook, 1995; Johnson et al., 1995; Liu et al., 1993; Liu et al., 1995) and validated using the personal monitoring data, to indirectly predict personal exposure. The models are poor predictors of personal exposure when only one outdoor and only one indoor microenvironment are factored into the model. The predictive ability of the models improves as more microenvironments are considered. The poor predictability of many models using ambient data is likely due to the poor relationship between outdoor and indoor ozone levels. Indoor ozone levels generally follow the diurnal pattern of ambient levels only in ‘leaky’ buildings. Most indoor microenvironments are ‘tight’, and indoor ozone levels remain low and quite flat.

Given the wide spatial and temporal variability in both ozone concentrations and time-activity, probabilistic models estimate exposure by combining all the principle elements of the source-to-receptor pathway. Specifically, pNEM uses detailed information on human activity patterns, indoor-outdoor ratios, and air exchange rates to predict how many days a “typical person” in a subpopulation cohort will be exposed above any given level during a specified exposure period. Outputs of the exposure model can be used to directly estimate population exposure by multiplying the outcome for the typical individual by the size of his or her cohort. The data are presented as frequency distributions for the general population, which include everyone who resides in the geogrqphic region being modelled.

By incorporating additional information about time-activity patterns, ventilation rates, and demographics into the exposure assessment, thus increasing the complexity of the input, exposure modelling indicates that a large percentage of the total population is exposed to ozone at concentrations greater than 82 ppb (the current Canadian Air Quality Objective). As would be expected, the predicted absolute number of person-days of exposure to the one-hour daily maximum and 8-hour average ozone is higher in regions with higher ambient ozone levels. Of the three cities modelled, person-days of exposure are greatest for Toronto residents, moderate for Montreal residents, and lowest for Vancouver residents.

Extrapolating the modelled results to the Canadian population leads to a prediction of greater person-days of exposure in southwestern Ontario, followed by southern Ontario, Montréal, the Southern Atlantic Region, and the Lower Fraser Valley. Exposure varies from year to year depending on time-activity patterns. During hot, sunny summers, time spent outdoors is greater, thereby increasing the likelihood of peak exposures. Not everyone, however, comes in contact with ozone levels measured at the FAMs. Therefore, when ambient data from FAMs are used to predict exposure, the total population living in the area has the potential to be exposed, but population exposure is usually overestimated.

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7 EFFECTS ON MATERIALS

Since the NO_x/VOC Assessment Program did not address the issue of ozone effects on materials, an independent review of the literature was undertaken. This review of ozone effects on materials is current to the end of 1996.

Although sulphur dioxide remains the most important pollutant in the degradation of materials, other atmospheric pollutants are gaining in importance as a result of declining emissions of sulphur dioxide. Ozone is one of these. As with other photochemical oxidants, ozone damages many types of materials both functionally and aesthetically. Ozone is sufficiently chemically active that even at low ambient concentrations the effect of material exposure to ozone can be observed (North Atlantic Treaty Organization (NATO), 1974). In the last ten years or so, it has become more apparent that that due to the high reactivity and complex chemistry of ozone, the effects of ozone on all materials can only be properly understood if one considers its interactions with other pollutants (ICP, 1996; Tidblad and Kucera, 1996; UN ECE, 1995). In addition, other atmospheric parameters such as temperature, sunlight and humidity can influence the impact of ozone on materials. Although the importance of these synergistic effects is noted, a full review of these effects is not appropriate for the purposes of this Science Assessment Document.

This chapter reviews the effect of ozone on elastomeric materials, textiles, dyes and pigments, surface coatings (paint) and metals and other building materials. Most of the research on the effects of ozone has been done on organic materials. Significant portions of this chapter are based on reviews by the United States Environmental Protection Agency (U.S. EPA,1996), the North Atlantic Treaty Organization (NATO,1974) and Lee, Holland and Falla, (1996) in the United Kingdom.

7.1 ELASTOMERIC MATERIALS

One of the earliest techniques used to assess ambient ozone was based on the consistent and rapid cracking of stressed rubber strips when exposed to ambient air. Either the time until cracking or the depth of cracking after a specified time could be related to ambient ozone concentrations (U.S. Dept. of HEW, 1970; Vega and Seymour, 1961). That cracking of rubber can be used effectively as an indicator of ozone concentrations has also been recently confirmed (Serano et al., 1993).

Elastomeric materials are long chain unsaturated organic molecules. Exposure of ozone to an elastomer results in a breakage of the molecular chain at carbon-carbon double bonds. One plausible effect mechanism is that ozone attacks elastomers by adding a chain of three oxygen atoms directly across the double bond, forming a five-membered ring structure. This structure rearranges to form a zwitterion and an aldehyde. The aldehyde-zwitterion pair can be formed on either side of the chain scission. Subsequent reactions of the zwitterion lead to a permanently oxidized elastomer (U.S. EPA, 1996). This mechanism of chain scissioning explains why saturated polymers such as silicones, ethylene, butyl rubber, and propylene are inherently resistant to ozone damage. In contrast, the effects of ozone on natural rubber, general purpose diene rubber, and synthetic polymers of polyisoprene, polybutadiene, acrylonile-butadiene and styrene-butadiene, can be extremely damaging due to their high content of main chain unsaturated carbons (Lee et al., 1996.). Polymers such as polyethylene, polypropylene, nylon, and polystyrene appear to be embrittled by high ozone concentrations (ozone concentration>1000 ppm), but at current ambient ozone levels, effects are not significant (Lee et al., 1996). Neoprene, on the other hand, is highly unsaturated, but is highly resistant to crack growth due to the electronegative chlorine atom adjacent to the double bond (Lee et al., 1996).

In an unstressed state, the chain scissioning only occurs to a shallow depth of 0.5 μm and appears as a white bloom or a surface frost (Lee et al., 1996). The reaction rate of ozone at the polymer surface is several orders of magnitude faster than in the bulk material. The rate constants at 20 ° C have been determined for several polymers and range from 1.2×10^{-2} L/mol·s for polyisobutylene, to 4.4×10^{5} L/mol·s for polyisoprene (Razumovski & Zaikov, 1983). Sub-surface elastomeric material can be accessed by ozone during the formation of surface cracks. Surface cracks, during contortion, will expose a fresh elastomeric inner surface which can subsequently be attacked by ozone. In a non-stressed state, sub-surface polymers are not susceptible to ozone, even when they are exposed to ozone for a long duration (NAT0, 1974). An exposure period of 16 hours to 1500 ppm ozone caused no observable effect in non-stressed natural and synthetic rubbers (Tucker, 1958).

Elastomers are usually used in varying degrees of stressed states. Tensile stresses of 2-3% are enough to make the elastomer vulnerable to ozone concentrations of 0.01 - 0.02 ppm. Cracks will appear perpendicular to the direction of the applied stress (Lee et al., 1996). As cracks deepen, elastomers mechanically weaken. It is also believed that some of the adhesive properties of certain rubbers are reduced (Lee et al., 1996).

Degradation of elastomers also occurs as a result of exposure to other pollutants and to natural weathering processes; in particular, to sunlight. The importance of these factors, relative to the effect of ozone, is an ongoing area of research (Lacoste et al., 1994; Tidblad and Kucera, 1996). Unfortunately, the damaging effects of sunlight can be difficult to distinguish from those induced by exposure to ozone (Yocum and McCaldin, 1968; Yocum and Upham, 1977).

Methods, such as the utilization of wax and antiozonant coatings, have been developed to protect elastomers from ozone degradation. Amorphous or microcrystalline and paraffinic waxes form a non reactive barrier between the ozone and the elastomer (Jowette, 1983). Wax coatings can be used more effectively in conjunction with antiozonants. An antiozonant forms a protective barrier in which the substance protects the elastomer, by itself reacting with the ozone. The most effective antiozonants are all N,N' derivatives of p-phenylenediamine (Lattimer et al., 1984).

There are currently two primary theories as to how antiozonants chemically protect polymers (Lattimer et al., 1984). 'The scavenger theory', suggests that antioxidant additives diffuse across the surface of the polymer, where they form a protective layer and react with the ozone sacrificially before the ozone scissions the double bond of the material (U.S. EPA, 1996). ‘The protective film theory’, also assumes a diffusion of the antiozonant to the surface of the polymers, but the protective layer is less reactive with ozone than the double bond, therefore sealing the double bond away from the ozone (U.S. EPA, 1996).

In addition to these two primary theories, other theories have been proposed. ‘Relinking theory’, predicts that the antiozonants are involved with the repair of the scissioned double bond (Lattimer et al., 1984). ‘Self healing film theory’, predicts that the antiozonant reacts with the daughter molecules formed from the ozonolysis, creating a low molecular weight inert film that prevents ozone from further penetration (Lattimer et al.,1984). It is likely that more than one protection mechanism is in operation in each situation (Lattimer et al., 1984).

Protective layers (the wax, antiozonant or laminant) are also subject to degradation. Antiozonants must diffuse to the surface of the elastomer to be effective, but in doing so they become vulnerable to external damage during normal usage such as abrasion. Oil, gasoline, and other chemical agents such as acidic deposition (Lee et al., 1996) may leach them (NATO, 1974). Removal of the antiozonant reduces ozone protection, therefore effectively decreasing the functional lifetime of the product.

Chemical protection of polymers from ozone can be improved via hydrogenation (the removal of the double bond with a substitution of a hydrogen atom) or the use of saturated polymers in the elastomers composition. The hydrogenation process is a complex time consuming process due to the material’s viscosity and the high molecular mass (Lee et al., 1996). The substitution of all unsaturated polymer materials for saturated ones to increase the resistance to ozone is not always viable. Substitutions may change the desired physical properties of the elastomer, such as resilience and resistance to stress relaxation. Applications for saturated polymer products are limited and presently they account for less than 10 percent of elastomer consumption (Lee et al., 1996).

Antiozonants appear to aid in the long term protection of elastomers, but once a first crack is formed, oxidation is likely to continue until component failure. Higher ambient temperatures increase diffusion of the antiozonant to the polymer surface (U.S. EPA, 1993), thus increased temperature aids the ozone protection of the elastomer. Fortunately, ambient ozone concentrations correlate well with high temperatures, when the antiozonant is most effective (U.S. EPA, 1996).

Table 7.1 lists the available concentration response studies. The lowest ozone concentration at which effects were observed on elastomeric materials is 0.02 ppm (20 ppb). At this level, cracks were observed in stressed vulcanized rubber strips after relatively short periods of time (Bradley and Haagen-Smit, 1951).

7.2 TEXTILES

Cellulose fibers (such as cotton or silk) can be affected by ozone via the same mechanisms as elastomers (unsaturated double bond cleavage). The degradation caused by ozone results in a reduction of the tensile strength and other physical properties. Degradation is indirectly assessed by measuring changes in textile fluidity (NATO, 1974).

Sunlight, heat, alternate wetting and drying, and micro-organisms are factors that also contribute to the weathering and deterioration of textiles. The effect of textile exposure to these factors (for example, when clothes are outside exposed to ambient air) is greater than the deterioration of fiber caused by ambient ozone (NATO, 1974). In general, the contribution of ozone to the degradation of fabrics has not been well quantified, but is considered insignificant (U.S. EPA, 1996). However, Bogaty et al. (1952) and others have demonstrated the synergistic effects of moisture and ozone on fabrics. Low levels of ozone can degrade fabrics if they are sufficiently moist.

Table 7.2 lists the available concentration response studies. The lowest ozone concentration at which effects are observed is 0.02 ppm (20 ppb) (Bogarty et al., 1952). At this level, the tensile strength and fluidity of duck and print cotton cloth is demonstrably reduced. However, these effects only occurred when the cloth was wet. Dry cloths exposed to 0.02 ppm ozone did not show any significant effects.

Table 7.1 Ozone effects on elastomers and polymers (adapted from U.S. EPA, 1996)

Material	**Concentration**	**Exposure Time/Conditions**	**Effect**	**Comment**	**Reference**
polyethylene polystyrene polypropylene nylon	1000ppm	-20 hour exposure in the presence of UV radiation -control was run under ambient ozone conditions of 20 ppb	-embrittlement	-it would take the control 114 years to achieve the same degree of embrittlement	Lee et al., 1996
automotive tires	0.25-0.5 ppm (ozone) 0.04 ppm (ambient air)	LABORATORY STUDY -no exposure time specified -tires were mechanically stressed FIELD STUDY -greater than 1 year exposure -actual service use	-cracking of white side wall	-there was a positive correlation between the laboratory test and the field test	Hofmann and Miller, 1969
vulcanized rubber strips	0.02-0.46 ppm and 20, 000 ppm (ozone)	-3 to 65 min exposure -material was mechanically stressed (100% strain by bending)	-surface cracking appeared in 1 sec. at high concs. and in 5 mins - > 1 hr. at low concs.	-dose–response curves were developed	Bradley and Haagen-Smit, 1951
rubber tires and various polymers	0.023 to 0.048 ppm (ambient air)	-150 to 700 hours exposure -physical stress -this was a field study (ambient air)	-time of cracking was observed	-cracking occurred over a broad range of values and was related to the stress	Meyer and Sommer, 1957
SBR: Plysar S and Plysar Krylene	0.25 ppm (ozone)	-19 to 51 hours exposure -temperature was 120 ° C -100% strain -test was conducted with and without antiozonants	percent of antiozonant was related to the cracking depth	-dose–response curve was developed on unprotected rubber	Edwards and Storey, 1959
polyisoprene	0 - 1.8 ppm (ozone)	-2 hour exposure -temperature was 22 ° C	-cracking and stress relaxation	-rates of attack were proportional to ozone concentration	Razumovskii et al.,1988 Cont.

Table 7.1 cont. Ozone effects on elastomers and polymers (adapted from U.S. EPA, 1996)

Material	Concentration	Exposure Time/Conditions	Effect	Comment	Reference
white side wall specimens	0.05 to 0.5 ppm (ozone)	-250 - 1000 hrs exposure -10 and 20% strain	-cracking rates were determined for varying stress and ozone concs.	-2 - 5 years of ambient air required for ozone cracks to penetrate cord depth	Haynie and al. 1976
10 different NR, SBR, and CR formulations	0.5 ppm (ozone)	-up to 300 hours exposure -temperature was 30 ° C -were tested with and without antiozonant protection	-time to 10% to 20% relaxation	-both formulation and protection affect relaxation	Ganslandt and Svensson (1980)
natural rubber, epoxidised rubber and co polymer	0.05 to 1000 ppm (ozone)	-16 hour exposure -20 to 70 ° C -10 to 100% strain	-time to first cracking	-temperature dependence of the antiozonants was observed	Lake and Mente (1992)
several NR/SBR blends, with and without protection	0.05 to 0.15 ppm	-3 to 16 hour exposure -sunlight -humidity	-interply adhesion affected at 0.05 ppm and above	-both antiozonants and waxes are needed for protection against sunlight plus ozone	Davies (1979)
tire cords (nylon 66; Dacron polyester; Kevlar aramid)	0 to 1.5 ppm (ozone)	-0 to 48 hour exposure -UV light -heat (100°C) -rh (20 to 90%) -NO_2	-RFL adhesion loss occurred primarily during 6 hour exposure to high rh and 0.2 ppm ozone	-synergism between ozone and rh -RFL deterioration occurred at the surface	Werghoefer (1974)

Table 7.2 Ozone effects on textiles (adapted from U.S. EPA, 1996 and NATO, 1974)

Material	Concentration	Exposure Time/Conditions	Effect	Comment	Reference
duck and print cotton cloth	0.02 ppm and 0.06 ppm	-50 days exposure -experiment conducted in absence of light -wet (≥50% moisture content) and dry cloths were exposed to ozone; wet cloths were also exposed to clean air	-reduction in fluidity and a 20% loss in tensile strength in ozone exposed wet samples -control cloths retained much of their tensile strength and fluidity	-ozone at low concentration can oxidize cellulose -ozone level more effectively degrade fibers if they are kept sufficiently moist (ozone is more soluble in water than air at room temperature)	Bogaty et al., 1952
print cotton cloth	0.5 ppm	-50 days exposure -absence of light -21°C, 72% rh	-no effect on fluidity or breaking strength	moisture content of cloth (9%) too low to produce degradation when exposed to ozone	Morris (1966)
print cotton cloth	0.75 ppm	-60 days exposure -absence of light -25°C -every 3 days half the samples were machine washed, the other half were soaked in water for 1 minute -control sample was not exposed to ozone -excess water was removed from all samples via a wringer system	-control sample showed no significant change in tensile strength -ozone exposed samples showed an 18% and a 9% loss in tensile strength for the machine and water soaked samples respectively	-the increased degradation of machine washed samples may have been due to the alkalinity of the detergent	Kerr et al., 1969 Cont.

Table 7.2 cont. Ozone effects on textiles (adapted from U.S. EPA, 1996 and NATO, 1974)					
Material	**Concentration**	**Exposure Time/Conditions**	**Effect**	**Comment**	**Reference**
modacrylic, acrylic, nylon 66, polyester	0.2 ppm	-7 days exposure -artificial sunlight -~39% rh -48 ° C -cloth wetting for 18 minutes every 2 hours -control was not exposed to ozone	-slight reduction in breaking of acrylic and nylon fibers as compared to the control -no change was observed for the modacrylic and polyester fibers	-synthetic fibers not as affected by ozone as the cellulose fibers	Zeronian et al., 1971
nylon yarn	0.03 ppm	-up to 445 days exposure -dye yarn with acid blue 45 and acid blue 122	-fibers lost ability to be dyed	-exposure to ozone affected the dye ability of the fiber	Makansi, 1986

7.3 DYES AND PIGMENTS

7.3.1 Textile Dyes

In the early 1900s, oxides of nitrogen were considered the major active fading agents. It was not until ‘o-fading’ (the bleached appearance of faded fabrics exposed to ambient air in areas of low NO_x) was observed, that a search for another oxidant capable of colour fading began (Salvin & Walker, 1955). The products most affected were cotton and polyester garments and nylon carpets. Ozone was identified as being the causal agent in the fading (NATO, 1974).

Many textile dyes react with ozone, causing the colour of the dye to fade. The colour change is the result of ozone molecules breaking the aromatic ring portion of the dye molecule, oxidizing the dye. The daughter molecules that result from this oxidation process can be differently coloured than the parent or colourless. Consequently, the original dye colours become altered or faded (U.S. EPA, 1996). With certain dyes, the effect of direct sunlight cannot be distinguished from that of ozone (Yocum and McCaldin, 1968; Yocum and Upham, 1977). As with impacts on the textiles themselves (section 7.2), ozone exposure alone fails to produce a large amount of colour fading. High moisture levels or relative humidity are also required. For example, when nylon carpet was subjected to ozone, humidity levels of at least 65% rh were required to produce pronounced colour fading. Generally, fading decreases rapidly below 65 % rh (NATO, 1974).

The chemical nature of the textile fiber and the dye can be used to predict the degree of ozone fading that is likely to occur. The chemical structure of the dye and the fiber determine the degree to which fiber and the dye remain associated. Ability of the dye to dissociate from the fiber, diffuse and migrate along the surface plane of the textile is directly related to the fading observed (Haylock & Rush, 1976).

Two important fiber characteristics in ozone-induced fading are the cross-section modification ratio and fiber draw ratio (orientation of the polymer chains) (Haylock & Rush, 1976). An increase in the modification ratio will increase the cross-sectional area and subsequently increase ozone penetration and fading. Increases in the draw ratio, however, will increase the number of fibers oriented in the same direction as the fiber polymer chains which decreases the amount of ozone-caused fading (Haylock & Rush, 1976).

Other factors that influence the dye degradation are: the manner in which the dye is applied, the presence of protective agents, ambient temperature, relative humidity, the presence of other air pollutants, and the amount of strain the textile fiber undergoes due to folding, creasing, and stretching and the chemical nature of the dye itself. Higher molecular weight dyes will diffuse more slowly than lower molecular weight dyes and subsequently, are less susceptible to ozone induced fading.

Certain combinations of dye type and textile type may increase immunity to ozone fading. Some dyes are inherently immune to ozone fading independent of the substrate textile. Studies have shown that ozone has no fading capabilities on royal blue acetate, red rayon-acetate, or plum cotton dyes (U.S. EPA, 1996). However, some combinations of textile and dye increase the fiber's susceptibility to ozone. Low ozone levels (0.02 - 0.05 ppm) are able to fade sensitive fibers such as red and blue dyes in cellulose acetate, viscose and cotton muslin (U.S. EPA 1996).

The available database on the effect of ozone on fabric dyes does not permit the derivation of meaningful dose-response relationships. Much of the literature is qualitative in nature, with little detail given as to ozone exposure concentrations. Comparisons among studies are difficult given that temperature and humidity conditions vary from one study to another and relative humidity is known to be an important factor in ozone induced fading. Nonetheless, there is clearly good evidence that exposure to ozone does induce fading (U.S. EPA, 1996).

Table 7.3 lists the available concentration response studies. The lowest ozone concentration at which textile dye impacts have been observed is 0.02 ppm (20 ppb) (Ajax et al., 1967). However, the concentrations in the Ajax et al. (1967) experiment are questionable (U.S. EPA, 1996). A more reliable LOAEL for effects of ozone on textile dyes is therefore 0.05 ppm (50 ppb). At this level, a large variety of dye - fabric combinations are prone to fading.

7.3.2 Artists Dyes

Ozone causes the degradation, particularly fading, of artists' pigments in paintings and other important cultural assets. In addition, where these pigments are applied to organic materials (e.g. paper), these too may be susceptible to the effects of exposure to ozone. Due to the uniqueness of works of art, these ozone-induced changes are considered unacceptable (U.S. EPA, 1996). Generally, artist dyes are part of cultural items, e.g., artworks, and are not typically exposed to ambient conditions, being protected in indoor environments. However, indoor environments are not devoid of ozone.

Given that art and museum collections are intended to be preserved for great lengths of time, most recommendations for the protection of such materials are for concentrations of ozone in the indoor air to be limited to 1 ppb ozone (Cass et al., 1991). The implications of this for the protection of outdoor art are significant, given that ambient ozone levels are generally far higher than this. Outdoor ozone concentrations can also be a major determinant of indoor ozone concentrations (see Chapter 6), depending on the building's ventilation system. Works of art that are subjected to high air ventilation rates in museums (2 or 3 air changes per hour) will encounter a higher dose of ozone and will subsequently experience greater degradation (U.S. EPA, 1996). Druzik et al. (1990) have found that in museums, art galleries and historical houses, the indoor / outdoor ozone ratio ranged from 0.10 to 0.87. Some fading has occurred in current collections, but it is not possible to distinguish light-induced fading from chemically-induced fading (Cass et al., 1991). The use of display cases (that are removed from normal air circulation) and framing behind glass provide some protection against fading. The use of ozone resistant pigment and coatings are encouraged to reduce the susceptibility (Cass et al., 1991).

The concentrations of ozone used to induce fading in controlled dose-response studies are higher than those that usually exist in ambient museum air, yet the results are arguably applicable to the issue of protecting art over the longer term (Cass et al.,1991). There is evidence from controlled exposure studies that the fading of artists' pigments in the presence of ozone is directly related to the product of exposure concentration x exposure duration. If true, then an art collection exposed to 0.001 ppm (1 ppb) of ozone for 100 years will be affected similarly (in terms of fading) as one exposed to 0.4 ppm (400 ppb) of ozone for 90 days (Cass et al., 1991). The latter exposure (400 ppb over 90 days) has been shown to produce severe fading of many artists' pigments (Shaver et al., 1983; Whitmore and Cass, 1988). This model is therefore potentially useful for evaluating the long-term effects of ozone, without long term experimentation.

Table 7.4 lists the available concentration response studies for artist pigments and dyes. The lowest concentration at which effects were observed in response to ozone exposure alone is 0.4 ppm. (This was also the lowest experimental concentration tested in these studies). At this level colour fading occurs in traditional organic colourants, Japanese colourants and various artist colourants in 95 days, according to a number of studies. Cass et al. (1991) found effects on alizarin crimson (on watercolour paper) in 7 days at an exposure of 0.4 ppm ozone.

Table 7.3 Ozone effects on textile dyes (adapted from U.S. EPA, 1996)

Dye	Textile	Concentration	Exposure Time/Conditions	Effect	Comment	Reference
blue & red	drapery	0.1 ppm	-no exposure conditions specified -dyes were tested with and without antiozonant	-dyes without antiozonant were markedly bleached while samples that contained antiozonant were not	-oxidants caused dye fading, not NO_x	Salvin and Walker, 1955
disperse	cellulose acetate	laboratory exposure to auto exhaust (approx. ozone conc. of 0.02 - 0.55 ppm field exposures not reported	-54 hours exposure -69 dye-fabric combinations -SO_2 was present in the reaction vessel -tests were conducted in rural and urban areas using light-proof cabinets 3 months exposure period	-photochemical by-products of irradiated auto exhaust caused more fading than non-irradiated samples or SO2 and clean air combination - a more than additive effect was observed for SO_2 + O_3 (lab. and field exposures)	-reported laboratory concentrations are questionable -temperature and humidity were not the primary cause of dye fading but were principal contributing fading factors (field exposures)	Ajax et al., 1967
direct, fiber reactive vat, sulphur, azo	cotton					
disperse	polyester					
disperse, basic	orlon					
disperse, acid	nylon taffeta					
direct	viscose					
premetolized, acid	wool					
direct red 1	cotton	0.05 and 0.5 ppm	-12 weeks exposure -temperature is 55°F and 90°F -50% and 90% rh	-both the 0.05 and 0.5 ppm ozone levels induced fading	-increased temperature and humidity increased the amount of fading, but ozone's effect appeared to be more dependent on high rh	Beloin, 1973
direct red 1	rayon					
acid red 151	wool					
reactive red 2	cotton					
basic red 14	acrylic					
azoic[b] red	cotton					
acid orange 45	nylon					
acid yellow 65	wool					
basic yellow 11	acrylic					
sulphur green 2	cotton					
acid violet 1	wool					
direct blue 86	cotton					
disperse blue 3	cellulose acetate					cont.

Table 7.3 Ozone effects on textile dyes (adapted from U.S. EPA, 1996)

Dye	Textile	Concentration	Exposure Time/Conditions	Effect	Comment	Reference
disperse blue 3	nylon					
disperse blue 27	cellulose acetate					Cont.
disperse blue 27	polyester					
reactive blue 1	cotton					
reactive blue 2	cotton					
vat blue 14	cotton					
AATCC O_3 ribbon	acetate					
olive I and II disperse blue 3 and 7	nylon	0.2 and 0.9 ppm	-1 to 6 hours exposure -70% to 90% -40 °C temperature	-linear fading dependent on [ozone], increased rh increases the amount of fading	-increased fiber characteristics such as draw ratio reduced fading -increases in fiber characteristics such as modification ratio increased fading -increased temperature increased the fading observed -increased fiber surface area increased fading	Haylock and Rush, 1976
disperse blue dye in an avocado green mixture	nylon 6 yarn	0.05 ppm	-time duration not specified -85% rh -temperature was 40 °C	-fading related with fiber surface area, namely the diameter		Huevel et al., 1978
2 disperse dyes, 2 acid dyes	nylon 6 and nylon 66 carpet	not specified	-3 months to 3 year time duration -experiment was conducted on 28 homes around the country	-geographic and seasonal variation was notice in the fading	-a field study experiment	Nipe,1981 Cont.

Table 7.3 Ozone effects on textile dyes (adapted from U.S. EPA, 1996)

Dye	Textile	Concentration	Exposure Time/Conditions	Effect	Comment	Reference
disperse blue 3	nylon 6 yarn	0.2 ppm	-time duration was 2 to 120 hours -65%, 85%, 90% rh -temperature was 40 ° C	-time caused a nearly linear increase in fading -fading rate was largely dependent on rh		Kamath et al., 1983
disperse, basic disperse direct vat, sulphur, fiber reactive disperse disperse, acid direct acid, mordant	acrylic cellulose acetate cotton polyester nylon viscose rayon wool	not specified	-time duration was for 2 years -time interval was every 3 month -experiment was conducted in light proof cabinets	-2/3 of the sample experienced significant ozone fading	-this was a field study at rural and urban sites	Beloin, 1972
disperse blue 3 Acid blue 25 Acid blue 40 Acid blue 45 Acid blue 80 Acid blue 127	nylon 6 and 66 yarn	0.2 ppm	-time duration 0 to 96 hours -85% rh -40 ° C	-fading proceeded consistent with diffusion of dye to fiber surface	-changes of the dye's morphology towards the production of a more compact fiber to reduce dye mobility and ozone fading -use of high molecular weight dies will slow down diffusion	Moore et al., 1984
royal blue red plum plum	drapery rayon acetate rayon acetate cotton duck	0.5 and 1.0ppm	-time duration 250 to 1000 hours -50% and 90% rh -NO_2 and SO_2 were added to the reaction vessel	-statistically relevant ozone fading did not occur	-this was a laboratory study -no synergistic relationships could be determined among pollutants	Haynie et al., 1976

Table 7.4 Ozone effects on artist dyes (adapted from U.S. EPA, 1996)

Material	Substrate	Concentration	Exposure Time/Conditions	Effect	Reference
17 watercolour pigments	paper	0.4 ppm	-time duration 95 days -temperature 23 ° C -47% rh	-only alizarin-based watercolours were very sensitive -all other pigments showed less fading	Shaver et al., 1983
alizarin, alizarin crimson, anthaquinone	silica gel, cellulose Teflon	0.4 ppm 0.4 ppm 10 ppm	-time duration 95 days -temperature 22 ° C -50% rh -time duration 18 - 80 hours -temperature 24 ° C -≤ 40% rh	-each pigment tested faded on all substrates	Grosjean et al., 1987
16 traditional organic colourants	paper	0.4 ppm	-time duration 12 weeks -temperature 23 ° C -50% rh	-11 colourants reacted while 3 possibly reacted of the 16	Whitmore et al., 1987
indigo, dibromoindigo, thioindigo, tetrachlorothioindigo	Teflon	10 ppm	-time duration 4 days	-all faded, but indigo and dibromindigo were consumed	Grosjean et al., 1988a
currcumin	cellulose, watercolour paper, silica gel, Teflon	0.4 ppm 0.4 ppm 0.4 ppm 10 ppm	-time duration 95 days -temperature 25 ° C -50% rh -time duration 4 days -temperature 24 ° C -≤20% rh	-all faded to colourless endpoints -water colour paper was slower to react	Grosjean et al., 1988b
traditional Japanese colourants and dyes	paper silk cloth	0.4 ppm	-time duration 12 weeks -temperature 22 ° C -50% rh	-several organic and one inorganic dye faded significantly	Whitmore and Cass, 1988

Cont.

Table 7.4 cont. Ozone effects on artist dyes (adapted from U.S. EPA, 1996)

Material	Substrate	Concentration	Exposure Time/Conditions	Effect	Reference
triphenylmethane colourants	Teflon	10 ppm	-time duration 4 days - temperature 24 ° C -$\leq$ 20% rh	-colourants with unsaturated carbons may fade	Grosjean et al., 1989
Alizarin crimson	watercolour paper	0.4 ppm	7 days 22°C and 50% RH dark	severe fading of unframed sample framed sample behind glass exhibited virtually no fading	Cass et al., 1991
various artists colourants	watercolour paper cellulose	mixture of: 0.02 ppm ozone 0.01 ppm PAN 0.08 ppm NO_2	-time duration 12 weeks -temperature 16 to 24 ° C -46 to 83 % rh -35 colourants were tested	9 colourants experienced substantial change, 11 colourants experienced negligible change, 12 colourants, small change and 3 colourants, modest change	Grosjean et al., 1993

7.4. SURFACE COATINGS (PAINT)

A surface coating is a material (paint, varnish or lacquer) which is applied to a substrate. It forms a coherent film for the intent of decoration or protection of substrates such as wood, metal, stone, plastic and composite substrates (Lee et al., 1996). A paint is a finely powdered pigment, dispersed in polymeric binder material which functionally holds the pigment to the surface (U.S. EPA, 1996).

Ozone has the ability to affect both the binder and the pigment in the paint, causing premature aging (ICP, 1996). The mechanism of deterioration is via the oxidation of the organic binder material similar to the mechanism of elastomeric degradation. The resulting damage is manifest as erosion (gradual weathering) of the paint, as well as cracking, peeling, and discolouration (NATO, 1974; U.S. EPA, 1996). Of these effects, erosion of the paint surface is the most studied with respect to air pollution effects. Discolouration arises from the oxidation of the pigment to daughter products which have a noticeably different colour or are colourless (U.S. EPA, 1996). The degree to which ozone will affect the paint varies by the type of paint, temperature, duration of wetness, wind speed, sunlight (Haynie & Spence, 1984), moisture and the concentration of other pollutants such as sulphur dioxide and nitrogen oxides (U.S. EPA, 1996). It is likely that the combination of these other factors will have a larger impact on the paint degradation than the degradation caused by ozone alone (Table 7.5).

Erosion of painted surfaces can be measured as a loss of weight, then converted to a loss of thickness of the paint coating; this approach has been used in some studies. However, there are recognized limitations to this approach, and it is evident that changes in weight of the surface coating may not arise solely from erosion of the binder and pigment in the coating (Lee et al., 1996). A number of damage functions for ozone-induced paint erosion have been reported in the literature, but the results are questionable (U.S. EPA, 1996). Haynie et al. (1976) exposed oil-based house paint, latex house paint, vinyl coating and acrylic coil coating to 0.5 and 0.05 ppm concentrations of SO_2, NO_2, and O_3, in different combinations. Significant ozone-induced damage to acrylic and vinyl coil coatings was observed, although the erosion rates were very slow. Analysis of the effect of ozone concentration on acrylic coil coating yielded a linear regression of

$$\text{Erosion rate} = 0.159 + 0.000714\,[O_3]$$

The calculated erosion rate is presented in micrometers per year, and $[O_3]$ is the concentration in micrograms per cubic meter (Haynie et al., 1976). Paint erosion from exposure to high ozone concentrations is predicted to be substantial by this linear relationship. However, at ambient ozone concentrations, erosion of paint is predicted to be insignificant. This linear regression predicts that a 20-µm thick coating would last over 80 years exposed to an average ozone concentration of 0.05 ppm (U.S. EPA, 1996).

Campbell et al. (1974) also studied the effects of ozone in combination with sulphur dioxide, on panels painted with different surface coatings (automotive refinish, latex coating, coil coating, industrial maintenance coating, and oil-based house paint). The panels were expose to low (0.1 ppm) and high (1.0 ppm) concentrations of ozone and sulphur dioxide over periods of approximately 0, 200, 350 and 500 days (Table 7.5). Significant increases in erosion rates were observed at high pollutant concentrations, with oil based house paints experiencing the largest increase (compared to control panels). The most ozone resistant coating was the automotive finish. However, ambient (0.1 ppm) concentrations of ozone did not produce statistically significant increases in erosion rates of any of the surface coatings (U.S. EPA, 1996) (Table 7.5).

Spence et al. (1975), (reviewed by Lee et al., 1996), also investigated the effects of combined exposures to ozone, sulphur dioxide, nitrogen dioxide and relative humidity on a number of paints. Both high and low exposures, and different exposure durations, were included in the study protocol. Although Lee et al. (1996) expressed some concern over the methodology used to measure erosion, the study was cited as providing evidence that high ozone concentrations (33 times urban background levels of approximately 15 ppb) are capable of eroding durable industrial coatings after about 40 days exposure.

Lee et al. (1996), extrapolating from the dose-response relationships of Campbell et al. (1974) and Spence et al. (1975), and assuming a linear dose-response relationship, were able to predict that in general, an increase in atmospheric ozone concentrations of 15 ppb, would result in an increase in the rate of erosion of between 1 and 2%, depending on the nature of the coating. The validity of this result was strengthened by the fact that the analysis of both the Campbell et al. (1974) and Spence et al. (1975) studies, which used different methodologies, yielded comparable results. The authors point out though that erosion is not the sole mechanism for degradation of surface coatings. Embrittlement, cracking, loss of adhesion, loss of gloss and soiling are all factors that should be taken into account (Lee et al., 1996).

Table 7.5 lists the available concentration response studies. The lowest ozone concentration that is supported by the concentration response data is 0.05 ppm (50 ppb). At this ozone concentration, there is a slow, observable erosion of coil coating (Haynie et al., 1976).

Table 7.5 Ozone effects on surface coatings (adapted from U.S. EPA, 1996)

Material	Concentration	Exposure Time/Conditions	Effect	Comment	Reference
latex and oil house paint, vinyl coil coating and acrylic coil coating	0.05 and 0.5 ppm (combinations of 0_3, NO_2 and SO_2)	-250, 500 and 1000 hour durations -50 and 90% rh -13 ad 35 ° C and artificial dew and sunlight cycles	-statistically significant ozone-caused damage on acrylic and coil coatings -very slow erosion rates of coil coating	-chamber experiment conducted with SO_2 and NO_2	Haynie et al. 1976
automotive refinish, latex, coil coating, industrial maintenance coating, oil house paint	0.1 and 1.0 ppm (0_3 and SO_2)	-up to 1000 hour duration -substrate was stainless steel panels -70% rh -temperature was 65 ° C -artificial dew and sunlight cycles	-1ppm ozone significantly deteriorated the finish -0.1ppm ozone did not significantly deteriorate the finish	-chamber experiment conducted with SO_2	Campbell et al., 1974
automotive refinish, latex, coil coating, industrial maintenance coating, oil house paint	ambient exposure; no pollutant measurements	-up to 24 month duration -substrate was stainless steel panels	-erosion was greater in polluted, urban areas	-field conditions for: • clean rural site • moderately polluted site • high SO_2 site • high NO_2 site	Campbell et al., 1974
oil-base house paint, acrylic latex house paint, vinyl coil coating, acrylic coil coating	0.08 ppm and 0.50 ppm O_3, in combination with high and low levels of NO_2 and SO_2	250, 500 and 1000 hour durations - 35 ° C - artificial dew and sunlight cycles - high (90%) and low (50%) RH	- oil-base house paint had the highest erosion rate - vinyl and acrylic coil experienced low erosion - latex house paint erosion rates were invalid due to reaction with SO_2	- chamber experiment - 16 different combinations of SO_2, NO_2, O_3 and RH at two levels	Spence et al., 1975
latex and oil house paint	0.006-0.055 ppm	-3 to 30 month time duration -substrate was stainless steel	-effects of ozone were not independently statistically significant	-field conditions at 9 sites in St. Louis	Mansfeld, 1980

7.5 METALS AND BUILDING MATERIALS

In contrast to its effect on organic materials (see previous sections), ozone on its own has little ability to affect inorganic materials (e.g. metals and building materials). However, the presence of ozone in a sulphur dioxide-containing environment accelerates the corrosion of zinc, silver, aluminum, nickel, iron, and copper, among other metals (Graedel et al., 1984; Druzik, 1985; Svenson and Johannson, 1993; ICP, 1996).

The work of Svenson and Johannson (1993) has shown that in the presence of ozone, the uptake of sulphur dioxide by zinc was greatly increased. In turn, this increased the amount of sulphate formed at the surface of the metal, thereby enhancing the corrosion process. The corrosion of zinc in the presence of ozone alone was negligible. The results indicated the ozone reacts with the loosely bound four valent sulphur on the surface of the zinc. The formation of the sulphate ion creates an electrolytic solution that has a corrosive effect on the protective surface oxide layer of the metal, exposing the underlying metal to corrosion. (The zinc corrosion layer, however, has much less zinc oxide (if any) than, for example, does a steel surface layer have iron oxides, given that zinc oxide produces zinc carbonate in the presence of atmospheric CO_2.) Although this study was limited to zinc, there is no reason to suppose that ozone accelerated, sulphur dioxide induced corrosion is restricted to zinc (Lee et al., 1996). Other metals may well be similarly affected.

Another interesting aspect of the work of Svenson and Johannson (1993) is that they were able to demonstrate that the acceleration of sulphur dioxide oxidation and deposition on zinc by ozone becomes greater as the sulphur dioxide concentration decreases. That is, as sulphur dioxide concentration decreases, the effect of ozone becomes increasingly important. This is significant given that, as authors Lee et al. (1996) have emphasized, sulphur dioxide and ozone concentrations are often out of sync, with sulphur dioxide peaking in wintertime, and ozone in the summer.

Ozone's effect on metals is influenced by environmental factors (e.g. temperature, humidity/wetness) in addition to the chemical composition of the atmosphere. Concentration-response relationships have been defined for steel, zinc, aluminum, copper, and bronze, for weight loss (WL in g/m^2) as result of studies conducted over a 4 year ozone exposure period. These clearly reveal the importance of the combined effects of both chemical and environmental factors (UN ECE, 1995):

- For weathering steel: WL = 85 + 0.26 TOW $[SO_2][O_3]$ + 432 TOW
- For zinc: WL = 14.5 + 0.043TOW $[SO_2][O_3]$ + 80 Rain $[H^+]$
- For aluminum: WL = 0.85 + 0.0028 TOW $[SO_2][O_3]$
- For copper: WL = 19.3+ 0.011 $[SO_2][O_3]$ + 162 Rain $[H^+]$
- For bronze: WL = 11.8 + 0.047 TOW $[SO_2][O_3]$

  Where $[SO_2]$ is the sulphur dioxide concentration ($\mu g/m_3$), $[O_3\ ]$ is the ozone concentration ($\mu g/m_3$). Rain is the amount of precipitation in m/yr, $[H^+]$ is the concentration, TOW is time of wetness or when rh>80% and temperature is greater than 0°C (represented as a time fraction of the duration of the exposure).

Stone is also subject to degradation outdoors as a result of exposure to both natural weathering and anthropogenic pollutants. Both SO_2 and NO_x are known to cause the deterioration of calcareous stone (ICP, 1996; Haneef et al., 1992). In the case of SO_2, the critical reactions are thought to involve an attack on either Ca (OH_2) or $CaCO_3$ by sulphuric acid, leading to the formation of gypsum, which can crystallize within the pores of the building material (ICP, 1996, Haneef et al., 1992). The oxidation of SO_2 to sulphuric acid involves water and the presence of atmospheric oxidants such as ozone. The degradation of building material by NO_x has received comparably less attention. The key reactions involve the oxidation of NO_x in the presence of water to form calcium nitrate (ICP, 1996; Haneef et al., 1992). The calcium nitrate formed is quite soluble, however, and may be quickly washed off the surface of the stone.

Marble, a natural stone, is widely used as a building material. The presence of ambient pollutants can accelerate the surface erosion of marble (Haynie et al., 1976) and lead to diminished aesthetic value. A concentration-response relationship has been developed from experimental studies to predict the erosion occurring on the surface of a marble structure:

$$E = -3.31 + 0.078\ rh + 2.95 \times 10^{-3}\ [SO_2] + 3.33 \times 10^{-3}\ [O_3]$$

where E is the erosion rate in ($\mu m/yr$), rh is the relative humidity (%), $[SO_2]$ is the sulphur dioxide concentration ($\mu g/m_3$) and $[O_3]$ is the ozone concentration ($\mu g/m_3$) (Haynie et al., 1976).

Again, clearly ozone is not acting alone, but in combination with other factors. Erosion rates predicted by this regression are quite low. If we accept that the results of an exposure over several weeks can be extrapolated to several centuries, then the erosion that is predicted from exposure to 0.03 ppm of ozone, and 0.03 ppm sulphur dioxide, over 300 years, is 1 mm of marble.

Haneef et al. (1992) used an atmospheric flow chamber to investigate and quantify the effects of SO_2, NO_2 and NO on a number of stone materials, both wet and dry. These pollutants were added as single exposures or in combination with ozone, to further understanding on the role of ozone as an oxidant in the chemical reactions occurring on building materials. Pollutant concentrations within the experimental chamber were 10 ppm, which allowed realistic presentation rates of the pollutants to be used. A 30-day exposure period and four different stone types were used (Table 7.6).

Dry stones showed little weight gain in the presence of SO_2, NO_2 and NO. In the presence of ozone, however, all stones showed a weight increase and often these were considerably greater than that which occurred in the absence of ozone (e.g. 6x greater than for NO and NO_2 alone on Portland limestone). All wet stones showed large weight increases after exposure to SO_2 and small weight losses after exposure to NO and NO_2 alone. Similar results occurred when O_3 was added to the experimental treatment. Weight changes of the wetted stones reflected the net result of chemical reactions and leaching of reaction products. Analysis of water-soluble anions revealed the presence of sulphates and nitrates, the amount of which was dramatically increased in the presence of O_3. The study was designed to investigate the mechanism of stone degradation and in particular the role of ozone in this degradation, but did not utilize a range of exposure concentrations that would allow formulation of concentration-response relationships.

Table 7.6 lists the available concentration response studies. The lowest ozone concentration at which effects can be observed cannot be identified due to the complex nature of ozone's synergistic relationship with SO_2 and NO_x. Experimentation involving a variety of co-exposures (varying each pollutant concentration independently) would aid the determination of an effect level.

Table 7.6 Ozone effects on metals and building materials

Material	**Concentration of Synergistic Components**	**Exposure Time/Conditions**	**Effect**	**Comment**	**Reference**
zinc surface covering galvanized steel	18 ppb SO_2 50 ppb O_3 50 ppb NO_2	-all 3 gases were tested separately and in various combinations -70% and 95% rh	-zinc was corroded far most effectively in combinations of NO_2 and SO_2, and O_3 and SO_2 than each gas separately -NO_2 and SO_2 combination was less corrosive than SO_2 and O_3 combination	-there is the suggestion of a synergistic relationship	Svennson and Johansson, 1993
copper	-various concentrations and combinations of NO_2, SO_2, and O_3	-humidified -25 ° C -another trial was run at a higher humidity of 75 rh	-reaction of O_3 alone with the copper produced CuO and $Cu(OH)_2$ which manifest as a decrease in the surface content of mono-valent copper	-synergistic effects of SO_2, and O_3 were more pronounced at a higher humidity - O_3 more effectively oxidizes SO_2 (to sulphate) than NO_2	Zakipour et al. (1995) (cited in Ortech, 1996)
White Cherokee marble	0.49 ppm and 0.098 ppm	-exposure time1000 hours -90% rh -temperature was 35 ° C -chamber study -synergistic effects of SO_2 and NO_x were studied	x-ray microprobe line scans revealed that sulphur penetrated the sample abut 50 µm -weight loss analysis showed erosion of up to 21.8 µm/yr	-ozone, in a high SO_2 atmosphere can erode marble	Haynie et al., 1976 Cont.

Table 7.6 cont. Ozone effects on metals and building materials

Material	Concentration of Synergistic Components	Exposure Time/Conditions	Effect	Comment	Reference
Pentelic marble Mansfield sandstone Massangis limestone Portland limestone	10 ppmv of SO_2, NO_2 and NO, alone or in combination with 10 ppmv of O_3	-time duration 30 days -84% rh -chamber study -both wet and dry trials were run	-the influence of ozone increased the degradation of the stone in all cases -wetted stones with pollutant gases and ozone gave the following order of reactions: $SO_2+O_3>NO_2+O_3>NO+O_3$ -the largest degradation occurred with wetted Portland limestone with SO_2 and O_3 which yielded a loss of 67.1 mg of calcium equivalents	-ozone reacts synergistically with other pollutants -wetting aids the synergistic effect soluble anions extracted from stones and run-off revealed the presence of sulphates and nitrates	Haneef et al., 1992

7.6 RESEARCH NEEDS

There is little question that ozone is affecting a variety of materials, alone and as a result of synergistic effects with other pollutants. There are clear causal mechanisms to account for the interaction of ozone at the molecular level with organic materials, and for the synergistic impacts of ozone and other pollutants on inorganic materials. For regulatory purposes, what is needed is a better characterization of concentration-response relationships. To date, there have only been a few investigations that have provided this type of information. Clearly this task is complicated by the synergistic nature of the reactions of ozone with other pollutants and environmental variables. Field studies, at ambient pollutant concentrations are required but clearly evaluation of such studies is complicated by the presence of multiple pollutants in the ambient air.

Useful information might nevertheless be obtained by choosing carefully exposure sites where climatic and pollution data are well known and where the concentrations of pollutants vary (Tidblatt and Kucera, 1996). If in addition, the experimental protocol involves exposing a range of materials that are known to react differently to the synergistic effects of different pollutants, the possibility of separating the effects of different pollutants (especially NO_x and O_3 since concentrations of these pollutants are usually highly correlated), is enhanced. Such a program is currently underway as a 4 year exposure progam under the UN ECE (1997-2001), based on the results of the previous 8 year UN ECE program (1987-1995). The new program includes a Canadian exposure site at the Dorser Research Center.

It is also very difficult to assess the existing database on the effects of ozone on materials because of differences in the methodologies employed in different studies, and differences in and difficulties with reporting the observed effects quantitatively (e.g. quantifying the degree of fading and cracking vs. a simple observation that fading or cracking appeared). Some standardization of procedures for investigating and quantifying the effects of ozone on different materials is required.

7.7 SUMMARY

Review of the literature indicates that ozone damages many different types of materials functionally and aesthetically. The damage is caused at the molecular level by chain scissioning and cross-linking mechanisms. In some cases there is an added synergistic degradation of materials due to the presence of other ambient pollutants, specifically sulphur dioxide and nitrogen oxides.

Among the stretched elastomer materials tested, natural rubber, general diene rubber, polyisoprene, polybutadiene, acrylonile-butadiene and styrene-butadiene were most affected by ozone. Neoprene, silicones, ethylene, butyl rubber and propylene were not observably affected by ozone. Protection of elastomers can be increased by the use of antiozonants and waxes.

Ozone has the ability to damage textiles by reducing tensile and break through strength. Among the textiles tested, cellulose fibers, such as cotton or silk, suffer the greatest tensile strength reduction when exposed to ozone, while synthetic fibers, such as acrylic, modacrylic, nylon and polyester, are not noticeably affected. Factors such as sunlight, heat, moisture and microorganisms can also cause reduction in tensile strength.

Ozone has the ability to fade or discolour dyes. Lower molecular weight anthraquinone dyes appear to fade most quickly while dyes such as royal blue (rayon-acetate), red (rayon acetate) and plum (cotton) were not observed to fade. A number of artist pigments were found to fade in the presence of ozone. Fine art dyes, such as in cultural exhibits, can be protected by limiting exposure to ozone or through the use of ozone resistant pigments or coatings.

Ozone has the ability to erode surface coatings by reacting with the binder and/or the pigment. High concentrations of ozone do cause paint erosion, although low (ambient) concentrations have little effect. Oil based house paints were most susceptible to ozone damage while automotive finishes and paints were the most ozone resistant. Other factors that contribute to paint erosion are temperature, moisture, sunlight, and the presence of other ambient air pollutants. These factors are considered to be of greater importance than ozone in affecting the erosion rates of paints and other surface coatings.

The impact of ozone on metal and building materials is primarily a result of synergistic effects with sulphur dioxide. The corrosion of metals, such as zinc, silver, aluminum, nickel, copper and iron is accelerated in the presence of both ozone and sulphur dioxide. Ozone alone appears to have little effect on metal corrosion. Stones materials, such as marbles, sandstone, limestones, bricks, concrete, and gravel, are also affected by synergy between ozone and sulphur dioxide.

Studies conducted in ambient air are prone to the variability of that environment. The variability in the concentrations of synergistic ambient variables could make interpretation of data increasingly difficult due to the complexity of synergistic relationships. Attempts were made in some laboratory studies to mimic the ambient environment, via the inclusion of some other variables (e.g., humidity, high temperature and UV penetration). At times, modelling was used to approximate damage that would occur in the ambient environment.

For the majority of materials examined, effects were reported qualitatively (e.g., fading/cracking). Even though concentration response relationships were identified for paints, metals and marbles, the way in which the effects of ozone were quantified was diverse (each relationship predicted either a quantified erosion rate, cracking, or weight-loss). Also, inconsistencies in mathematical expression of the relationship (e.g., linear, and synergistic) hampered the merging of the results into an overall concentration response relationship for materials.

The effect levels demonstrated for the different material types are listed in Table 7.7. It should be noted that these effect levels were by and large obtained under very specific laboratory conditions and are not necessarily representative of real world conditions. No effect level was determined for metals and building materials due to the complex nature of synergistic relationships with sulphur dioxide and nitrogen oxides.

Table 7.7 Lowest Observed Adverse Effect Level (LOAEL) for Ozone Effects on Materials

Material	Lowest Observed Adverse Effect Level	Experimental Conditions
elastomers	0.020 ppm (20 ppb)	5 mins., mechanically stressed
textiles	0.020 ppm (20 ppb)	50 days, wet cloths
textile dyes	0.050 ppm (50 ppb)	12 wks., 50% and 90% RH, 55° F and 90° F
artist dyes	0.4 ppm (400 ppb)	7 days, dark, 22 and 50 % RH
surface coatings	0.05 ppm (50 ppb)	250, 500 and 1000 hrs., O_3 in combination with SO_2, NO_2, 50 and 90% RH
metals and building materials	not determined	not applicable

Ozone impacts on elastomers and textiles were observed at levels as low as 0.020 ppm (20 ppb), while the lowest concentration at which impacts on textile dyes and surface coatings were observed was 0.050 ppm (50 ppb). Although the lowest observed concentration at which effects were noted on artists' dyes was .4 ppm (400 ppb), this concentration induced severe fading of the artists' dye. Further, Cass et al. (1991) have proposed that evidence exists for effects on artists' dyes to be a function simply of exposure concentration x exposure duration. Given the long periods of time over which artists' works require preservation, it is likely that effects would be observed at much lower concentrations if sufficiently long exposure durations were considered.

Recognizing the variability of confounding contributions of other atmospheric parameters (light, temperature, relative humidity and other air pollutants), it is not possible to define a single lowest observed effect level for the effect of ozone on materials. The data suggest that the level above which ozone effects are demonstrated on materials is in the range of 20-50 ppb, and that the effects observed at this level may be exacerbated by the presence of other atmospheric parameters.

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