LIGHT DUTY VEHICLE EMISSIONS AND THE OXIDANTS ISSUE IN CANADA

Pollution Measurement Division Environmental Protection Service Environment Canada

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## NOTICE

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prepared by Pollution Measurement Division Environmental Protection Service Environment Canada

#### 1 Ozone Impacts in Canada

Of all the routinely monitored air pollutants in Canada, it is ozone that gives the most cause for concern. In a number of urban and rural areas of Canada, measured levels are frequently exceeding those concentration values that have been demonstrated to have adverse effects on human health, crop productivity and forest growth.<sup>1</sup>

Canada can be divided into four zones of ozone impact based on the frequency of occurrence of levels in excess of the federal one-hour acceptable and tolerable air quality objectives and on the mean ozone concentration during the growing season.

- (a) The south-western portions of Ontario and Quebec (i.e., the corridor stretching from Windsor to Quebec City). The one-hour tolerable air quality objective for ozone is regularly exceeded, and mean growing season concentrations are above the threshold for forest and crop effects<sup>2,3</sup>. Approximately 40% of Canada's population resides within this zone and the commercial value of ozone-sensitive crops growing in Ontario alone exceeds \$650 M.
- (b) Vancouver and the lower Fraser Valley. The one-hour tolerable air quality is frequently exceeded<sup>4</sup>; mean growing season concentrations are above the threshold for forest and crop effects. Maximum hourly concentrations have reached 265 ppb, a concentration higher than the Los Angeles first-stage episode level at which health advisories are issued.
- (c) The provinces of Nova Scotia and New Brunswick. The one-hour acceptable air quality objective is frequently exceeded and the one-hour tolerable objective is occasionally exceeded.<sup>5</sup> Mean growing season concentrations are close to but below the threshold for crop and forest effects although the current monitoring data base is limited.
- (d) The remainder of Canada. The one-hour acceptable air quality objective for ozone has been exceeded at most urban sites where monitoring has been carried out.<sup>6</sup> Exceedances are expected at rural sites, based on U.S. data, but little monitoring has been carried out.

Given that concentrations of ozone in major areas of Canada are unacceptable because of health and economic effects, consideration must be given to control actions. Development of an optimum ozone control strategy, however, must take into account precursor emission sources, photochemical formation mechanisms and meteorological influences.

#### 2 Source/Receptor Relationships

Photochemical oxidant pollution was thought at first to be strictly an urban problem and early studies focused mainly on the Los Angeles basin.<sup>7</sup> In more recent years it was discovered that elevated ozone concentrations also occur in rural areas and that ozone episodes can occur over regional scales approaching 1000 km.8,9,10,11 Regional episodes have also been shown to be associated with specific synoptic scale meteorological conditions.<sup>12,13</sup> Ozone concentrations measured at any location can be the result of the superposition of ozone originating from a number of different sources including ozone from natural sources, ozone from urban plumes and ozone undergoing long range transport from distant source regions.<sup>14</sup> Within Canada, southwestern Ontario and Quebec are most affected by long range transport ozone episodes with ozone transport from the United States strongly implicated. Elevation of the regional ozone concentration occurs downwind of Toronto and Montreal, 12, 13 due to precursor emissions from those cities. In the Maritimes long range transport of ozone is the dominant mechanism leading to ozone episodes, with local emissions playing an apparently insignificant role.<sup>5</sup> In Vancouver and the Fraser Valley, emissions from Vancouver are the major contributor to the ozone problem.<sup>4</sup>

2.1 Precursor to Photochemical Oxidant Formation. Ozone is a secondary pollutant formed primarily from emissions of volatile compounds (VOC) and nitrogen oxides  $(NO_x)$  although other compounds such as carbon monoxide (CO) play a role. The total amount of oxidant formed depends on the amount of organic reactants available. These can transform nitric oxide to nitrogen dioxide, and thus disrupt the NO<sub>2</sub>-NO-O<sub>3</sub> equilibrium that would otherwise exist. The photochemical formation processes producing ozone also generate a number of other secondary reaction products such as hydrogen peroxide, nitric acid, formaldehyde, peroxyacetyl nitrate (PAN), etc. Because ozone can be measured more easily than the other photochemical products, ozone concentrations are used as an indicator or surrogate for all oxidant compounds.

The majority of emissons of both  $NO_X$  and VOC in Canada come from the transportation sector, with light duty vehicles the largest single contributor.<sup>15</sup> Within the major metropolitan areas light duty gasoline vehicles contribute 25 to 40% of the total VOC and  $NO_X$  emissions (see Tables 1 and 2). Other major sources of VOCs include petroleum refining and marketing, heavy duty vehicles and application of surface coatings. Other major sources of  $NO_X$  include thermal power, industrial and commercial fuel combustion and diesel-fuelled engines.

TABLE 1 PERCENTAGE OF TOTAL VOC EMISSIONS BY SOURCE SECTOR	(1978)
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Source Sector	Vancouver	Toronto	Montreal
Transportation			
Light Duty Vehicles	38%	40%	27%
Heavy Duty Vehicles	11	8	4
Other	9	7	5
Fuel Combustion	1	1	1
Industrial Processes			
Petroleum Refining	12	5	31
Other	2	4	7
Miscellaneous			
Gasoline Marketing	14	16	12
Surface Coatings	7	11	7
Other	6	8	6
TOTAL EMISSIONS (t/y)	95 700	176 500	224 500

Studies conducted in a number of airsheds in Canada and the United States have indicated that relatively large reductions in precursor emissions would be needed to achieve compliance with air quality objectives. For example, in Los Angeles it has been calculated that an 85% reduction in VOC emissions would be required to achieve the U.S. standard of 0.12 ppm. Current control efforts in the Los Angeles basin will result in only a 33% reduction in VOC emissions and a 23% reduction in NO<sub>x</sub> emissions by 1987.

Source Sector	Vancouver	Toronto	Montreal
Transportation			
Light Duty Vehicles	34%	27%	25%
Heavy Duty Vehicles	11	6	5
Diesel Engines	23	19	23
Other	12	8	7
Fuel Combustion			
Power Generation	1	16	1
Other	16	21	29
Industrial Processes			
Petroleum Refining	3	3	8
Other	-	-	1
TOTAL EMISSIONS (t/y)	68 900	165 500	142 300

TABLE 2PERCENTAGE OF TOTAL NOx EMISSIONS BY SOURCE SECTOR (1978)

However, this level of control is expected to reduce the number of first stage episodes by 27% and reduce peak ozone levels from 400 ppb to 290 ppb.16,17

To achieve the required VOC and  $NO_X$  reductions in any air shed, mobile source emission reductions must be an integral part of the overall control plan. Generally, VOC controls are less expensive to implement than  $NO_X$  controls<sup>18</sup> but of the available  $NO_X$  control options, mobile source controls are generally the most costeffective. For VOC control options, the relative cost-effectiveness of mobile source controls depends largely on the nature of the other emission sources in the area. Generally, mobile source controls are of the same cost magnitude as other major source VOC control options.

2.2 Photochemical Models. A well designed emission inventory is required to provide the information needed to make decisions regarding air management strategies. However, it is only in combination with a mathematical treatment of the processes of dispersion, transport and chemical transformation (i.e., a model) that a link between changes in source emissions and measured receptor concentrations can be made.

Models may be broadly classified on the basis of the spatial scale (i.e., urban or regional) which they treat, and according to the complexity of the mathematical treatment of the processes of dispersion, transport and chemical transformation. The more complex a model, the more detailed the input data must be.

Because U.S. control strategies have focused on urban areas, it is urban scale models that have been most generally applied in studies of oxidant control strategies.<sup>19</sup> However, most urban scale models do not address multiple day episodes within the urban area or down-wind effects of the urban area emissions. Further, there appears to be no general acceptance of quantitive model outputs, even for intensely studied areas such as St. Louis and Los Angeles.<sup>20,21</sup> In spite of this, the urban scale models have been the basis for U.S. control strategy implementation plans.<sup>22,23</sup>

Regional scale and long range transport (LRT) models for ozone, incorporating all required elements of transport, diffusion, daytime and nighttime photochemistry, etc., are not yet available, although a number are under development.<sup>24</sup>,<sup>25</sup> These models are clearly needed for realistic control strategy development in areas affected by transported ozone but it will be a number of years before they can be applied and the outputs studied.

The major problem regarding the application of any model in Canada, be it urban or regional, is the lack of an adequate data base. A major effort will be needed to improve emission and ambient monitoring information especially for VOCs. However, available models could be adapted and applied to give an indication of the effect of control actions rather than to determine a quantitative source/receptor relationship.

### 3 Control Strategy Development

A Canadian control strategy for ozone and other photo-chemical pollutants should be geared towards reducing concentrations in the two most impacted areas of Canada, namely the Vancouver-Fraser Valley region and the Windsor-Quebec City corridor.

An optimum control strategy will have to recognize the different nature of the ozone problem in each area. As noted earlier, the Vancouver ozone problem stems from locally generated emissions. In general, maximum concentrations occur on days when stagnant synoptic meteorological conditions and high inland temperatures cause the seabreeze. Emissions from the downtown and suburban areas are transported east by the light sea-breeze flow. Maximum concentrations occur at the most eastern monitoring stations. The extent of the downwind effects of Vancouver emissions on crop growing areas of the Fraser Valley is not currently known nor are the influences of day-to-day

carryover of ozone and precursors during multi-day episodes. Visibility reduction is also a significant feature of ozone episodes in the area.

For the Windsor-Quebec City corridor, long range transport of ozone is often a dominant factor in measured concentrations. Episodes frequently encompass a large part of the region and can include New York state. The existence of an ozone "bulge" downwind of Toronto has been well documented and it can be anticipated that a "bulge" also exists downwind of Montreal. Ozone episodes usually occur with a stationary high over the eastern seaboard of the U.S. Flows are from the southwest with moderate to strong winds. Trajectory analyses indicate that major U.S. source regions include Michigan, Ohio, Indiana, New York and Pennsylvania. Air masses moving to Montreal often pass through Ontario.

Although the nature of episodes in the two regions is different, data analysis clearly shows that high ozone levels are occurring frequently and that the severity and duration of ozone episodes pose real threats to human health and property. Data trends do not indicate any amelioration of the situation and positive actions to improve the air quality of the regions are indicated.

As discussed earlier, the only quantitative way of linking planned emission reductions to reduced oxidant impacts is through the application of a model. Clearly, models are required for each area which can replicate ozone episode conditions and show the effect of abatement strategies. Unfortunately, as has been noted, directly applicable models are not available nor are the emissions and air measurement data bases adequate to support model development. The models and data bases will in fact require at least six to seven years to complete even if high priority and significant resources were to be assigned immediately. It appears that any contemplated control strategies will have to address the qualitative aspects of source receptor relationships rather than the quantitative aspects. In this context, it is worthwile to examine some of the controversies surrounding the selection of an optimum control strategy for ozone.

3.1 NO<sub>X</sub> vs VOC Control. Since both NO<sub>X</sub> and VOC emissions are implicated as precursors of photochemical oxidants, it would be logical to assume that control of both would be the most effective way of reducing oxidant concentrations. Unfortunately, the situation is not that simple and a good deal of controversy revolves around the choice of VOC control, NO<sub>X</sub> control, or both VOC and NO<sub>X</sub> control as an optimum strategy.<sup>26</sup>

Essentially, the entire scientific community agrees that reducing VOC concentrations will reduce ozone levels. The U.S. Environmental Protection Agency's policy, developed in 1971 and updated in 1976, was to control VOC alone to reduce oxidants.<sup>23</sup> NO<sub>x</sub> controls were adopted for the sake of reducing NO<sub>x</sub> effects and not necessarily because of NO<sub>x</sub> influence on photochemical oxidants. The VOC-only control policy, however, was based on the premise that oxidants were an urban air pollution problem and that local ozone concentrations were the result of local precursor emissions. The discovery of the rural ozone problem and the link between urban emissions and rural ozone concentrations through long range transport changed the picture entirely. Clearly, urban control strategies could not be addressed independently of the rural and regional effects of these strategies.

A great deal of effort, especially since 1976, has been expended in the U.S. to determine the effectiveness of implemented and planned control strategies. Studies have been carried out in the field and in smog chambers with a variety of results, claims and counter-claims. The most widely accepted beliefs can be summarized as follows:

- For single-day urban episodes caused by locally generated emissions, VOC control alone is the most effective way to reduce ozone for urban atmospheres with typical VOC/NO<sub>X</sub> concentrations. Reductions in VOC will not cause a linear decrease in ozone.<sup>27</sup>
- 2) For single-day episodes, NO<sub>X</sub> reductions at constant VOC concentrations can at certain VOC/NO<sub>X</sub> ratios lead to increased ozone concentrations within urban areas.<sup>28</sup> NO<sub>X</sub> emissions initially act as an ozone scavenger and zones of ozone depletion exist near large NO<sub>X</sub> sources such as roadways. The zone of depletion is small but probably affects a large number of current ozone monitoring sites. NO<sub>X</sub> increases will delay the formation of the ozone maximum and may displace the zone of maximum concentration to a further downwind location.<sup>29,30</sup>
- 3) For multi-day episodes the situation is not clear, with the general feeling that VOC controls will have less impact on ozone maximums within an urban area and even less impact downwind. Multi-day episodes are much more difficult to simulate and/or model. The effect of NO<sub>x</sub> controls on multi-day eposides is very uncertain.<sup>31</sup>
- 4) Reducing NO<sub>X</sub> in urban areas will likely reduce ozone concentrations in downwind rural areas. At high VOC/NO<sub>X</sub> ratios such as those existing in most rural areas ozone producton is limited by the amount of NO<sub>X</sub> available.<sup>31</sup>
- 5) For transport situations where incoming ozone concentration to the urban area to be controlled are high, VOC or NO<sub>X</sub> reductions will have little effect within the urban

area but should reduce ozone maximums downwind. Regional reductions in VOC and  $NO_X$  should reduce the ozone forming potential of transported air masses.31,32,33,34

6) NO<sub>X</sub> and VOC reductions will reduce the concentrations of secondary products such as sulphates, PAN, nitric acid, acrolein and nitrosamines within and downwind of an urban emission area.<sup>31,33,34</sup> Initial NO<sub>X</sub> has been shown to be transformed almost entirely into PAN and nitric acid at rates up to 16-19%/h.<sup>35,36</sup>

Scientific agreement on optimum control strategy is prevented in large part by disagreements on the limitations of modelling and lab experiments (field and lab studies often do not agree) and because of incomplete characterization of many photochemical reaction initiators, intermediaries and products.<sup>37</sup> The photochemical and meteorological parameters affecting ozone formation are numerous and complex and many are beyond our measurement capabilities. Lack of adequate historical emission inventory data has hampered efforts to correlate emission trends with ambient concentration trends<sup>24</sup>,<sup>38</sup> and lack of studies on the health and environmental impact of photochemical pollutants other than ozone hampers efforts to address the impact of control of these in any cost-benefit analysis.<sup>39,40</sup>

**3.2** Stratospheric Ozone. The issue of stratospheric ozone contributions to the ozone problem in urban and rural areas must be addressed for the purpose of more accurately estimating the benefits to be derived from anthropogenic emission reductions.

There is no question that injections of ozone-rich air from the stratosphere can cause elevations of ground level ozone concentrations which can at times cause the hourly air quality objective for ozone to be exceeded. $^{41},^{42},^{43}$  These instances, however, are rare and isolated occurrences. More typially stratospheric ozone contributes less than 35 ppb to the daily average ozone burden and 20-45 ppb to maximum hourly averages (i.e., 30% of maximum tolerable hourly concentration level). $^{41},^{42},^{43}$  Although stratospheric ozone alone rarely causes levels in excess of air quality objectives, there is speculation that it can initiate photochemical reactions and should be included in model simulations.

3.3 Biogenic Organic Emissions. Rural oxidant concentrations were at first ascribed to organic emissions from vegetation. Early attempts at emission inventories indicated that on a continental basis, biogenic organic emissions were considerably larger than those from man-made sources.<sup>44,45</sup> The finding that terpenes were highly reactive also led some researchers and politicians to the conclusion that the ozone problem was due to natural emissions.<sup>46</sup> As in the case of stratospheric ozone, an answer to the

question of the importance of biogenic emissions is needed to estimate the benefits of anthropogenic emission controls.

The current state of knowledge regarding this issue can be summarized as follows:

- Current biogenic organic emission estimates are probably overpredicted<sup>47</sup>; calculated emissions do not agree with ambient air measurements. Ambient measurements are considered more reliable.<sup>48,49</sup>
- 2) All areas that have been investigated showed very low levels of biogenic hydrocarbons. Biogenic organics are not significant in urban areas.<sup>48,49</sup>
- 3) Biogenic organics are of a comparable reactivity to a typical urban mix of anthropogenic organics. Rural areas are low in  $NO_X$  and ozone is not likely to form through photoxidation of biogenic organics. They may act as ozone sinks rather than sources.<sup>46,50,51</sup>
- 4) Biogenic organic emissions may be relevant during long range transport of polluted air mass and should be addressed in any long range transport model for ozone.

**3.4 Transport.** The concept of long range transport of ozone is now generally accepted by the scientific community. Ozone aloft, in the absence of fresh precursor emissions or contact with the ground is quite stable and can be transported for considerable distances.<sup>5</sup> The occurrence of regional eposides of elevated ozone are well documented especially in the northeastern part of the United States and Canada.<sup>3,4,8,14</sup>

The phenomenon of ozone transport is of course important in explaining rural ozone and in determining the necessity for regional control strategies. Although transport is accepted, it is not perfectly understood and a number of important questions remain related to the maximum range of ozone transport and the influence of fresh local emissions on ozone maximums during transport.<sup>22</sup>

**3.5** Selection of a Control Strategy. Natural ozone concentrations resulting from stratospheric injections and photo-oxidation of biogenic emissions contribute approximately 35 ppb to long-term average ozone concentrations and do not normally play a significant role in the formation of peak ozone conentrations in urban and rural areas. Progress towards attainment of air quality objectives will only be possible through anthropogenic emission controls.

Because most of eastern Canada is subject to long range transport of ozone, with local emissions adding to the ozone burden, the optimum strategy should include control of both local  $NO_X$  and VOC emissions. As noted in Section 3.1 this strategy would

have the most impact on reducing rural ozone levels, on reducing the concentrations of other reaction products such as nitric acid, sulphates and PAN and on reducing the effect of a province's emissions on downwind areas. If both  $NO_X$  and VOC emissions were controlled, there would be no urban area increases in ozone which would be thereotically possible with  $NO_X$  control alone. Reductions in U.S.  $NO_X$  and VOC emissions also appear warranted to reduce impacts in eastern Canada; however, it must be noted that U.S. emission standards for  $NO_X$  and VOC for both mobile and stationary sources are already more stringent than those in Canada. The U.S. appears to be moving away from a strictly urban-oriented oxidants control strategy to a more regional strategy that will address rural effects.

For the other most affected area of Canada, the Vancouver-Fraser Valley, reduction of both VOC and  $NO_X$  emissions would appear to be the most effective approach. Again no local urban increases in ozone should result.

#### 4 Summary

It has been noted that, based on our knowledge of measured ozone concentrations and demonstrated effects, photochemical oxidant air pollution is an issue of immediate concern in the Canadian environment. It is also apparent from the foregoing discussions that any attempts at the present time to quantitatively relate precursor emissions to changes in receptor concentrations are not likely to succeed. Quantitative answers may be available in 6 to 10 years but it is unlikely that even these will be free of doubt or uncertainty. Given the time required to implement most control measures (5 to 10 years) a decision at this time to not take any action to reduce ozone concentrations would imply another 10 to 20 years of current or increased effects. It is felt that there is enough evidence available now to take action based on the qualitative aspects of source/receptor relations for ozone. The most logical course of action, especially for eastern Canada, is to reduce both  $NO_X$  and VOC precursors and hence reduce the photochemical oxidant impact due to local emissions. The reduction of ozone will be only one benefit of reducing emissions; the reduction of a host of other photochemical products such as nitric acid, PAN, nitrates, sulphates, aldehydes and organic acids should also occur.

Because the light duty gasoline vehicle is the largest single-sector contributor to total VOC and  $NO_X$  emissions in Canada, control of this sector must be addressed as part of any overall control strategy. However, the control of this source alone will not reduce ozone concentrations to acceptable levels throughout the major impact areas. For Vancouver, a major reduction in emissions of VOC and  $NO_X$  from all sources will be needed, a reduction likely beyond the capability of present best practical control technology. For southeastern Canada, an intensified U.S. control effort for VOC and  $NO_X$ as well as reductions in domestic emissions will be needed. Even though reductions in emissions of VOC and  $NO_X$  from light duty vehicles will not by themselves result in achievement of ozone air quality objectives, they will reduce ozone peak concentrations and mitigate ozone effects.

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