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A STUDY OF RELATIONSHIPS BETWEEN ISOPRENE, ITS OXIDATION PRODUCTS, AND OZONE, IN THE LOWER FRASER VALLEY, BC

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Abstract—As part of the Pacific '93 Oxidant Study that took place in the summer in the Lower Fraser Valley of British Columbia, we conducted measurements of isoprene, and its oxidation products methyl vinyl ketone (MVK) and methacrolein (MACR) at a surface site about 40 km east of the city of Vancouver. Hourly measurements were conducted between 16 July and 10 August 1993. The data indicated evidence for substantial contributions of isoprene chemistry to the production of ozone during oxidant episodes in this region. Maximum concentrations of isoprene, MVK, and MACR were 5.3, 2.0, and 1.0 ppb, resp., for 4 August. Analysis of the relationship between MVK and O_3 during the oxidant episode period 1–6 August led to an estimated contribution of isoprene chemistry of ozone production of $\geqslant 13\%$. The average measured ratio of MVK/MACR was about 1.9–2.0 in the daytime, compared to the published relative yield of 1.4. Comparison of the MVK and MACR measurements to those of organic nitrates led to the conclusion that there is a significant non-photochemical source of MVK and MACR in this urban area. © 1997 Elsevier Science Ltd.

Key word index: Isoprene, tropospheric ozone, oxidation products, methyl vinyl ketone, methacrolein.

INTRODUCTION

The Lower Fraser Valley (LFV), B.C., which contains the city of Vancouver at the mouth of the Fraser River (see Steyn *et al.*, 1997, this issue), is one of the regions of Canada that occasionally experiences levels of ozone in excess of the Canadian Air Quality Objective (AQO) of a 1 h average not greater than 82 ppb. Such episodes typically exist under the influence of high-pressure systems that lead to subsidence inversions, confining the anthropogenic emissions of the O_3 precursor VOCs and NO_x to a relatively shallow ($\approx$ 500–700 m) mixed layer. On average, there are 7 days per year in which the AQO is exceeded in the LFV (CCME Report, 1991).

In terms of anthropogenic ozone precursors, the LFV offers a relatively attractive case for study, in that Vancouver is an isolated urban environment where transport of VOCs and NO_x from outside the non-attainment area is likely to be unimportant. Detailed emission inventories are available for VOCs and NO_x emitted from both mobile and stationary sources. The LFV also contains substantial vegetation in the form of deciduous and coniferous trees as well as agricultural crops. Therefore, during warm and sunny summer days, emissions of natural hydrocarbons such as isoprene may represent an important source of reactive VOCs. In this light, the LFV area can be considered an urban forest environment. It has been shown that ozone production for other forested urban environments, in particular Atlanta, can be significantly impacted by isoprene chemistry (Chameides, 1988; Cardelino and Chameides, 1990). Although the relatively cooler temperatures in the LFV might be considered to lead to lower isoprene levels, the diversity and density of vegetation in the LFV could possibly counter that same effect. It has been shown that ozone production in a variety of rural areas of Canada can be dominated by isoprene chemistry (Lin *et al.*, 1991; Jobson *et al.*, 1994).

In July and August of 1993 the Atmospheric Environment Service of Environment Canada organized and conducted a four week field study of the meteorological and chemical factors leading to elevated ozone levels (and diminished visibility) in the LFV. This study involved aircraft-based measurements of key photochemical and meteorological variables, as well as enhanced monitoring of chemical species at surface sites. In this paper we discuss our measurements of isoprene, methacrolein (MACR), and methyl vinyl ketone (MVK) at the Harris Road surface site located about 40 km east of the Vancouver city centre.

Laboratory studies have shown that MVK and MACR are two of the dominant products of the OH-initiated oxidation of isoprene (Tuazon and Atkinson, 1990; Paulson *et al.*, 1992). Although measurements of isoprene provide useful information regarding the potential for isoprene's contribution to ozone production, concentration–time profiles of its oxidation products MVK and MACR provide a more direct measure of the actual rate of oxidation of isoprene, which can then be related to isoprene's contribution to ozone production. This is particularly true in the LFV, where nighttime outflow events tend to efficiently remove pollutants from the valley (Banta *et al.*, 1997, this issue); thus, daytime pollutant concentrations measured in the LFV represent the result of short time scale chemistry and/or emission. In this paper we discuss our measurements of these three reactive biogenically-derived VOCs over the period 16 July–10 August 1993. The measurements were conducted using a PC-automated solid-sorbent concentration/injection system coupled to a GC/MS instrument for separation and detection. The measurements clearly indicate the importance of isoprene as an ozone precursor in this region, at least for the oxidant event that was encountered.

EXPERIMENTAL

Concentrations of isoprene, MVK, and MACR (and other carbonyl compounds) were determined at the Harris Road site (49°15′N, 122°40′W) east of the Vancouver city center, from hourly samples obtained between 16 July and 10 August 1993. The measurements were conducted on-site employing an automated sample concentration technique involving preconcentration on Tenax-TA adsorbent and using capillary GC/MS for separation and detection. The collection technique is a modification of that previously described by Yokouchi (1991). A schematic diagram of the sampling system is shown in Figs 1a and b. As shown in the figure, ambient air is pumped, at known flow rate using a calibrated mass flow controller (Tylan), through a ≈ 5 cm length of 1/8″ stainless-steel tubing that is packed with ≈ 0.05 g Tenax TA (35/60 mesh). In the sampling mode (Fig. 1a) the Tenax sorbent trap is cooled to 15°C, using thermoelectric cooling chips. For most samples the components of interest were concentrated in the Tenax bed from a 300 cm^3 sample volume, collected at $\approx 30\ cm^3$/min. (corresponding to a 10 min integration time). The sample air was first drawn through a ≈ 10 cm tube packed with crystalline KI to remove O_3 from the sample. We found that without this trap, O_3 levels of 25 and 115 ppb lead to MACR losses of 13 and 59%, respectively. Other olefinic compounds are expected to be affected in a similar manner. Laboratory tests with gas-phase samples have confirmed that all of the analytes of interest are quantitatively transmitted through this KI trap.

Tests using gas-phase samples in the laboratory indicate that there is no breakthrough of the analytes from the Tenax trap for a 300 cm^3 sample. Tests in the field for real samples, in which we alternated between 300 and 500 cm^3 samples, confirmed this (i.e. there was no significant difference in the determined concentrations for different sample volumes). However, a large portion of the data obtained in July was from 800 cm^3 samples, for which the isoprene breakthrough was significant. The breakthrough behaviour of the Tenax trap was subsequently characterized at relative humidities of 10–80%; it was found that at 800 cm^3 the average deviation in response from the non-breakthrough case was -48%. Accordingly, a correction factor (1.48) was applied to that isoprene data. Although this adds to the uncertainty in this portion of the data, the resultant concentrations are in good agreement with other concurrent isoprene measurements at the site (Bottenheim *et al.*, 1997, this issue).

Sample constituents were desorbed from the Tenax trap by rapidly heating the trap to 250°C under He carrier gas flow, with the six-port valves positioned as shown in Fig. 1b. The analytes are then swept from the trap onto the head of the analytical column, a 0.32 mm × 10 m Poraplot Q capillary column (Hewlett-Packard (HP)), contained within a HP 5890 GC, maintained at an initial temperature of 40°C. At this temperature, the analytes are effectively trapped in a narrow band at the head of the column, even though the injection process occurs over a period of 10 min. The column is then temperature programmed at 15°C min^{-1} to a final temperature of 220°C. The eluting peaks are detected using an HP 5972 Mass Selective Detector (MSD). The MSD was operated in a scanning mode, from $m/e = 35$–160. However, peak areas were measured and analytes quantified using appropriate selected ion chromatograms.

In the sampling mode, periodic ($\approx$ twice/day) analyses of standard samples of acetone in air (at the 7 ppb level) were performed using the acetone permeation device shown in Fig. 1. The standard gas-phase sample is generated by switching the position of the top six-port valve shown in Fig. 1a, and diluting the output of the permeation source with clean air at $\approx 2.5\ \ell\ min^{-1}$. From the known output of the permeation source (GC Industries) and the total flow rate, the gas-phase acetone concentration is readily obtained. The sample flow rate and volume is approximately the same as for ambient samples; the bulk of the flow exits from the vent to ensure that the sample is at ambient pressure. The output of the permeation source was determined independently using the DNPH impinger method, according to procedures described in Sirju and Shepson (1995). The permeation rate was found to be 64.2 ± 3.7 ng min^{-1} through experiments both before and after the field study; the certified output level was 70.0 ± 2.1 ng min^{-1}. For quantitation, the relative instrument response to equimolar amounts of acetone (for $m/e = 58$) and each analyte (for the appropriate selected fragment of the molecular ion) was measured. The relative response factors were obtained from both directly injected dilute solution phase standards, and from gas-phase standard samples (prepared in Teflon bags) that were sampled exactly as for ambient samples. For all analytes the relative response factors obtained by the two methods were not statistically significantly different. These experiments were performed both prior to and following the field study to ensure that the instrument response had not changed over the course of the study.

Isoprene, MVK, MACR, and acetone were quantified using $m/e = 67$, 55, 70, and 58, respectively. For each sample chromatogram the selected integrated ion current was compared to that for a known quantity of sampled acetone (from the on-site gas-phase standard samples), and the absolute amount of the analyte is then obtained from use of the determined relative response factors. The detection limits for isoprene, MVK and MACR were 10, 100 and 100 ppt, resp., for 0.3 ℓ samples.

Measurements were conducted hourly, from ambient air samples that were drawn through a Teflon-filtered inlet placed ≈ 1 m above the roof of the mobile laboratory at the Harris Road site. The inlet was ≈ 4 m above the ground level. The inlet line was 1/4″ FEP Teflon tubing. For each sample, the overall analytical uncertainty was calculated from the statistical sum of all uncertainties associated with each component of the calculation (i.e. relative MS response factors, average absolute instrument response to acetone (determined from a running average of six consecutive

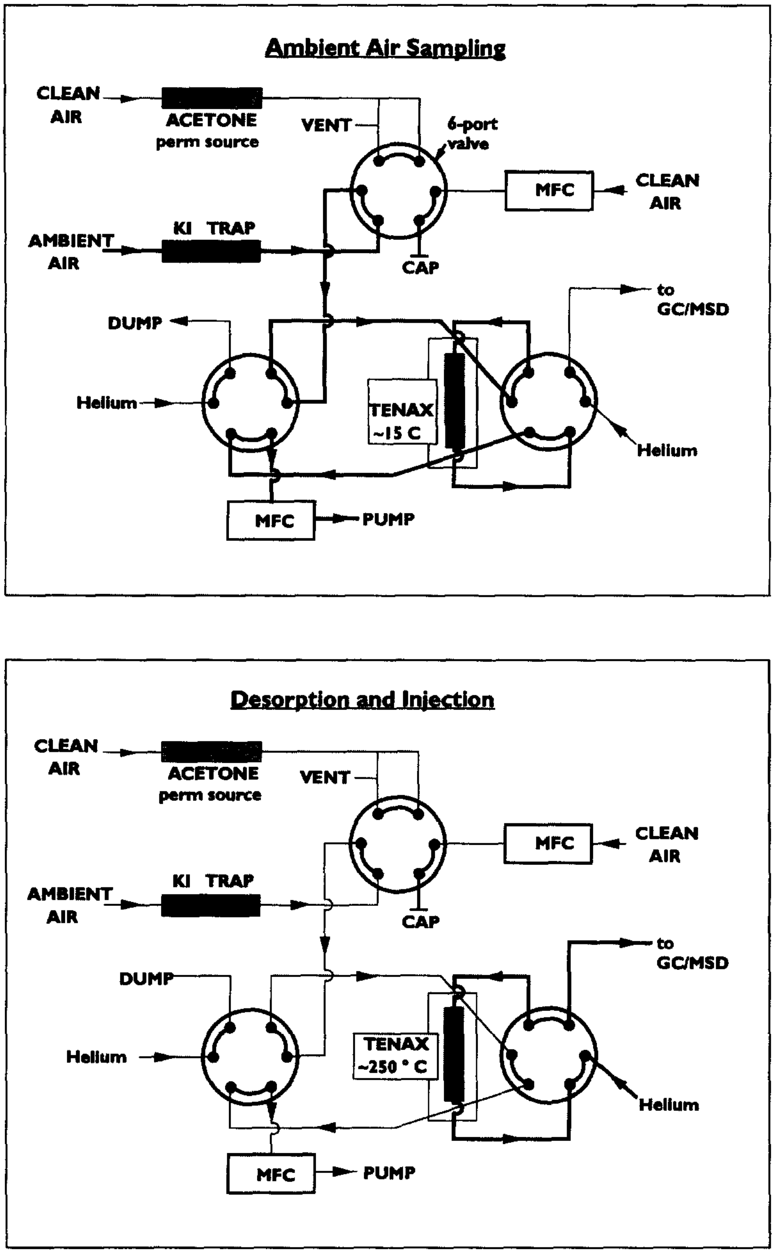

Fig. 1. Schematic diagram of sampling and injection system.

on-site gas-phase standard samples), blank levels (also a running average), and permeation source output). At the Harris Road site, canister samples were periodically obtained and analyzed for a variety of NMHCs, including isoprene, as described by Bottenheim *et al.* (1997, this issue). HCHO was measured at this site using Tunable Diode Laser Absorption Spectroscopy (TDLAS, Harris *et al.*, 1986). Organic nitrates were measured as described by O'Brien *et al.* (1997, this issue).

RESULTS

A detailed error analysis for the conditions of the measurements, i.e. including the observed variability of the blank levels, led to average overall uncertainties for our isoprene, MVK, and MACR measurements of ± 13, 28, and 27%, respectively. The slope of a regression of our isoprene measurements against those of Bottenheim *et al.* (1997, this issue) was 0.93 (± 0.05), and $r^2 = 0.94$. The average difference between the two sets of measurements was 35% (for $N = 21$). The isoprene, as well as O_3, measurements for the entire measurement period are shown in Fig. 2. The period 1–6 August was characterized by a high-pressure system lying off the western coast of Vancouver Island, leading to higher temperatures, relatively low daytime mixing heights ($\approx$ 600 m) due to subsidence, and

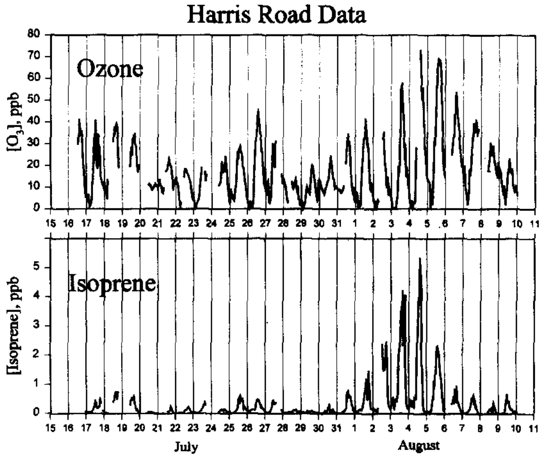

Fig. 2. Isoprene and ozone measurement data for the entire study period.

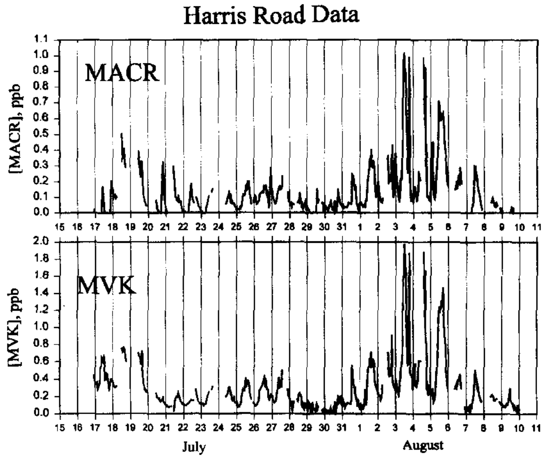

Fig. 3. MVK and MACR measurement data for the entire study period.

generally higher levels of pollutants, including ozone and isoprene. The maximum isoprene levels reached 5.3 ppb on 4 August when ozone also reached the maximum values observed during the study. The MVK and MACR data for the entire study period are shown in Fig. 3. The observations indicate relatively large concentrations of the isoprene oxidation products over the period 3–5 August, with maximum values of 2.0 and 1.0 ppb, resp., for MVK and MACR on 3 August. It is interesting that the maximum levels for MVK and MACR were observed on the 3rd, while the isoprene and ozone maxima were observed on 4 August. These data indicate not only that significant amounts of isoprene were present during the 1–6 August period but also that the extent of isoprene oxidation was substantial. As a result, we will focus our analysis for this paper on the 1–6 August period, with the aim of assessment of the contribution of isoprene to the production of ozone.

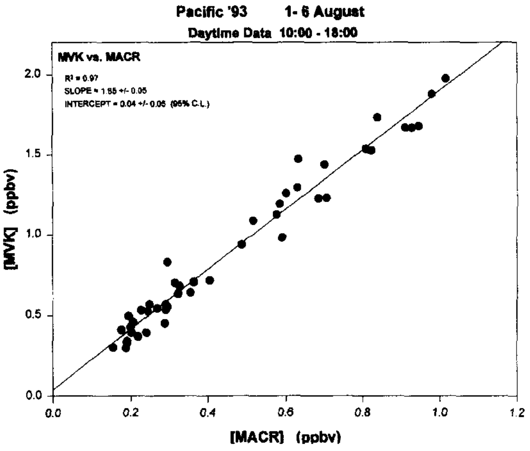

Fig. 4. Regression of MVK vs MACR for daytime data.

Since MVK and MACR are believed to originate largely from isoprene oxidation, and since the relative production yields are reasonably well known (Tuazon and Atkinson 1990; Paulson *et al.*, 1992), it is instructive to examine the relationship between these two compounds. A regression of the observed MVK vs MACR data from the episode period is shown in Fig. 4, where only daytime (1000–1800) data are used to remove the influence of the relative nighttime removal processes. The observed slope was 1.85 ($\pm$ 0.05), and $r^2 = 0.97$. The observed good correlation between these two species enhances our confidence in the data quality. The relative production rate has been found to be 1.4 (Tuazon and Atkinson, 1990; Paulson *et al.*, 1992). That the observed ratio is larger than that predicted from laboratory studies has been rationalized by Montzka *et al.* (1993) as resulting from the fact that consumption of MACR via reaction with OH is faster than OH reaction with MVK (by a factor of 1.66; Atkinson, 1989). However, it is interesting to note that we find a consistent ratio of about 1.9 $\pm$ 0.1 in the morning (0900–1200) periods of the episode week, when production is much faster than destruction. A plot of the diurnal average of the MVK/MACR ratio obtained by calculation of the average MVK/MACR ratio for all measurements obtained within each 1 h period is shown in Fig. 5. As shown in the figure the daytime average ratio is ≈ 2.0, in accord with the observations of Montzka *et al.* (1993) for a forest site in Alabama and of Yokouchi (1994) for a semi-rural site in Japan. However, in contrast to these other observations, this ratio appears to increase slightly at night in the LFV. Part of this difference could be due to the very low nighttime O_3 concentrations resulting from titration via reaction with NO, i.e. loss of MVK and MACR via O_3 reaction is much less important for the nighttime in Vancouver. However, it also appears that there are other sources of MVK and MACR, as discussed below.

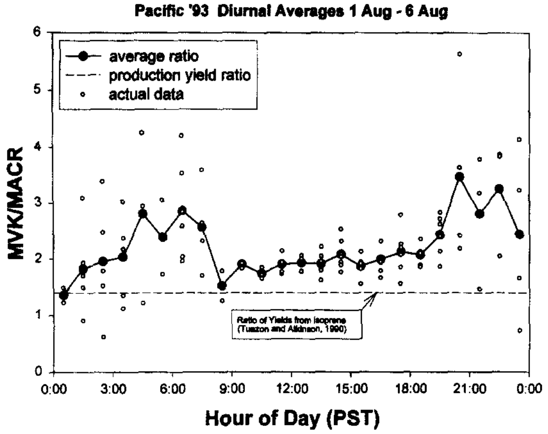

Fig. 5. Diurnal average of the MVK/MACR ratio.

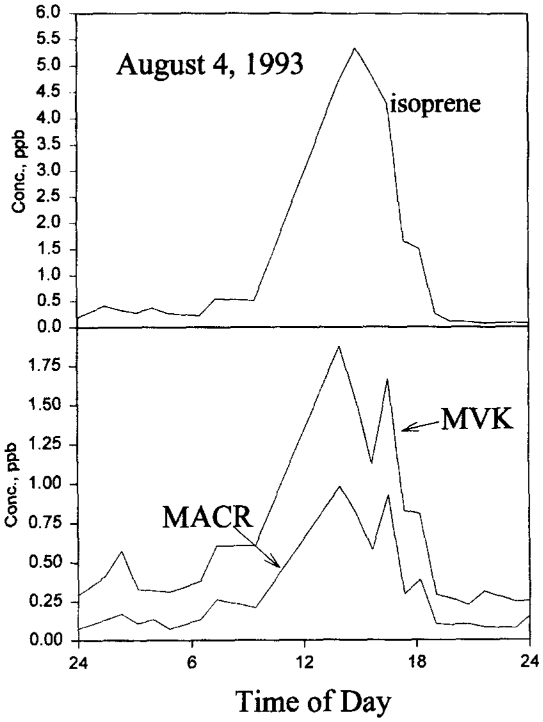

Fig. 6. Measurement data for isoprene, MVK, and MACR for 4 August.

One observation common to nearly all measured species is that there is a rapid "clean-out" of the lower Fraser Valley at night. This is demonstrated in Fig. 6, which shows the data for isoprene, MVK, and MACR for 4 August. At night, there is a substantial amount of drainage flow down the nearby mountains and past the Harris Road site toward Vancouver Island. As discussed in Banta *et al.* (1997, this issue), this drainage flow air is very clean, in part due to "scrubbing" of the pollutants from the drainage air as it flows through the mountain-side vegetation. The result is that between about 1800–2000 (on average), the Lower Fraser Valley pollutant concentrations decrease at an apparent rapid rate of about 25% h^{-1}. However, isoprene was observed to decay much faster than other species. For most species the decrease in concentration has been attributed to deposition in the katabatic outflow (Banta *et al.*, 1997, this issue). As discussed in Banta *et al.*, there could be a small contribution to the isoprene decay from the reaction with NO_3. However, our modelling studies indicate that for typical evening values of $[NO_2]*[O_3]$, NO_3 levels will be too low for isoprene loss via NO_3 to be a dominant removal mechanism.

DISCUSSION

Reaction of OH radicals with isoprene leads to MVK and MACR as major products. In each case, HCHO is produced simultaneously (Tuazon and Atkinson, 1990) in equivalent yield. Thus, if HCHO in the LFV is produced largely from isoprene oxidation, we would expect these isoprene oxidation products and HCHO to be highly correlated. A regression of HCHO vs MVK, for the 1–6 August episode period (daytime only) is presented in Fig. 7. This plot shows that these two species are in fact reasonably well correlated, with a regression slope of 4.4, and r^2 value of 0.88. If all HCHO were derived from isoprene oxidation, the slope would be 1.7 (assuming a 60% yield for HCHO; Tuazon and Atkinson, 1990). The

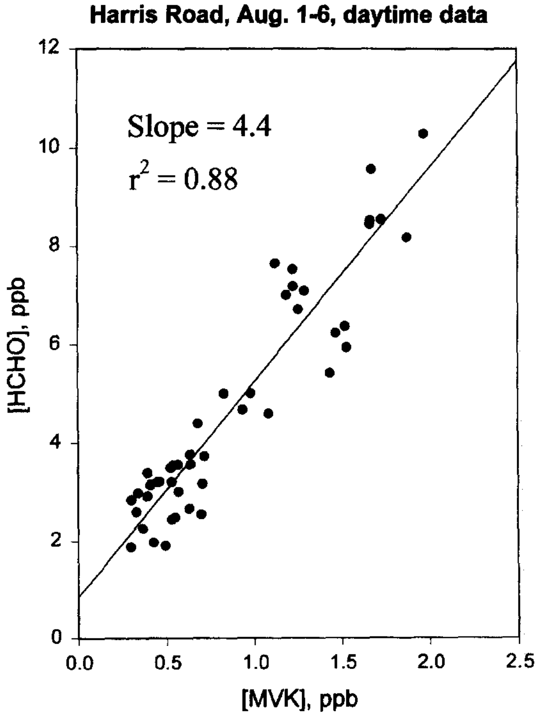

Fig. 7. Regression of HCHO vs MVK for daytime data.

data indicate that as much as 39% of the HCHO produced during oxidant episodes results from isoprene oxidation, in this urban environment. This analysis is not affected by secondary decay of these oxidation products, in that HCHO and MVK have nearly identical atmospheric lifetimes. Furthermore, as shown in Fig. 3, this is a period characterized by rapid photochemical *production* of these species, and the regression slope will be driven by the rapid change in concentration observed over a period of a couple hours at roughly noon each day. Li *et al.* (1997, this issue) find that about 70% of the daytime HCHO production at this site is from photochemistry.

Since isoprene emissions are dependent on temperature and radiation (Fehsenfeld *et al.*, 1993), and oxidant production also occurs under warm, sunny and stagnant conditions, we would expect isoprene to be correlated with its products. However, the regressions of isoprene against its products MVK and MACR show a rather weak correlation ($r^2 = 0.45$ and 0.41, resp. for 1000–1800 PST). This poor correlation may result from the fact that it is possible to have isoprene emissions, but low OH concentrations (i.e. slow oxidation). However, it is interesting to note that the regressions (not shown) show a significant possitive intercept for both MVK and MACR. The best-fit regression equations were $[\mathrm{MVK}] = 0.25(\pm 0.04)[\mathrm{isoprene}] + 0.43(\pm 0.19)$, and $[\mathrm{MACR}] = 0.13(\pm 0.02)[\mathrm{isoprene}] + 0.22(\pm 0.10)$, where the indicated uncertainties were the 95% confidence intervals. That there are statistically significant concentrations of these two compounds in the limit of zero isoprene concentration implies that there may be sources of MVK and MACR in the LFV other than isoprene oxidation.

Further evidence for a non-photochemical source of MVK and MACR can be seen in Fig. 8, in which we present the observations for the ratio $\{([\mathrm{MVK}] + [\mathrm{MACR}])/[\mathrm{isoprene}]\}$ during the 1–6 August period. As shown in the figure, this ratio is large in the evening and early morning, when the nocturnal boundary layer tends to trap emitted species in a shallow layer near the ground, and amplifies the impact of directly emitted species. Furthermore, this ratio is ≈ 1–1.5 at noon. This contrasts with the observations of Montzka *et al.* (1993) and of Yokouchi (1994), who report ratios in the range of ≈ 0.3–1.0. However, the interpretation of this ratio is difficult, as this ratio can be large as the *result* of photochemistry, as OH chemistry consumes isoprene, and produces MVK and MACR.

A better means of investigating the question of whether there are non-photochemical sources of MVK and MACR is to examine their concentrations against an indicator of photochemical activity. A good photochemical indicator is the concentration of organic nitrates ($RONO_2$). Organic nitrates are produced as a result of OH reaction with hydrocarbons, in the presence of NO. They are known to have only photochemical sources (Roberts, 1990). As discussed and presented in O'Brien *et al.* (1997, this issue), we measured a series of alkyl and multifunctional organic nitrates at the Harris Road site. Essentially all of the organic nitrates measured at the site are believed to be locally produced from alkane and alkene oxidation (O'Brien *et al.*, 1997, this issue); daytime production is rapid, and the nighttime outflow air tends to remove those alkyl nitrates produced during the day. Thus, the observed alkyl nitrate concentrations can be regarded as a direct measure of *local* scale hydrocarbon photochemical oxidation processes. A regression of MVK and MACR against the total alkyl nitrate concentration is shown in Fig. 9. Again, there are statistically significant non-zero intercepts (at the 95% CL) for both MVK and MACR (0.33 and 0.15 ppb, resp.), suggesting a background concentration of these compounds in the absence of photochemistry. The ratio of the two intercepts, 2.2, is consistent with that found from the regression of these species concentrations against isoprene.

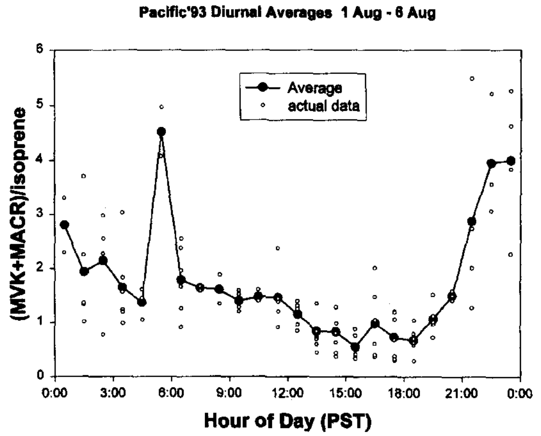

Fig. 8. Diurnal average of ([MVK] + [MACR])/[isoprene] for 1–6 August.

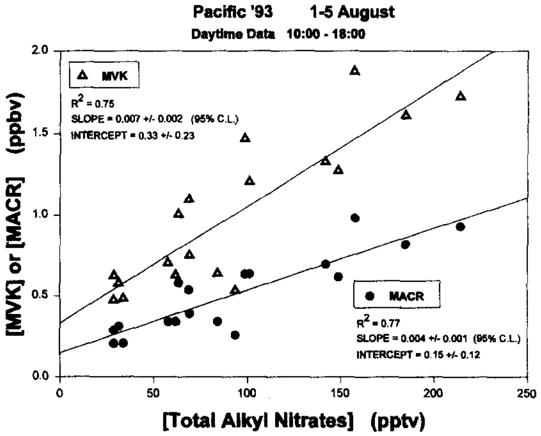

Fig. 9. Regression of MVK and MACR vs alkyl nitrates for daytime data.

One likely source may be direct emission from automobile exhaust. There is evidence for the formation of MACR from the combustion of *i*-butene (Ingham *et al.*, 1994) and for the formation of MVK from the high temperature oxidation of 1,3-butadiene (Brezinsky *et al.*, 1984); both *i*-butene and 1,3-butadiene are known components of automobile exhaust (AQIRP Technical Bulletin, 1992). A field and laboratory study by Jonsson *et al.* (1985) indicated that MVK and MACR are directly emitted from several types of vehicles and fuels, in roughly comparable quantities. MACR has also been measured by other researchers as an exhaust component in the combustion of gasoline and other test fuels (Kaiser *et al.*, 1993, 1994; Siegl *et al.*, 1992). The data in Fig. 9 imply that MVK may be emitted from vehicles, on average, at approximately twice the rate of MACR, since these intercepts clearly indicate the presence of MVK and MACR in the absence of hydrocarbon oxidation products. Recent measurements (unpublished data; manuscript in preparation) at our laboratories in Toronto in winter show the presence of low concentrations of MVK and MACR that are correlated with CO, and that they are present at an [MVK]/[MACR] ratio of roughly 2. We thus believe that there is a significant non-photochemical source of these two compounds, most likely automotive. This fact helps to explain why the MVK/MACR ratio does not decrease at night in Vancouver, in contrast to the observation of Montzka *et al.* (1993) for a forest site where direct anthropogenic emission of these carbonyl compounds would not be important. The PCA study of Li *et al.* (1997, this issue) using these data indicates direct emission of MVK and MACR in the ratio of 1.73 (MVK/MACR).

As discussed below, a substantial amount of the ozone production in the LFV is the result of isoprene oxidation. A useful test of the quality of the models used to simulate O_3 production in the LFV would thus come from a comparison of modeled MVK and MACR concentrations. However, in order to simulate these species properly, an automotive component of MVK and MACR would need to be included in the model emissions. We note that a similar plot of HCHO vs alkyl nitrates yields an intercept of 2.3 ppb. Not surprisingly, the automotive source is important for HCHO in the LFV. Relative non-photochemical sources of various carbonyl compounds are discussed in more detail in O'Brien *et al.* (1997, this issue) and Li *et al.* (1997, this issue).

An important question that has a large impact on ozone regulatory issues is the extent to which isoprene (or other natural VOCs) oxidation contributes to ozone production. In the presence of sufficient NO, as isoprene is oxidized, ozone as well as its oxidation products MVK and MACR are simultaneously produced. Therefore, it is possible to directly relate the production of MVK and MACR to ozone production from isoprene oxidation, taking into account the relevant product yields. The isoprene oxidation mechanism, consistent with the experiments of Tuazon and Atkinson (1990) and relevant to this discussion, is shown in reactions (1)–(4) below:

$$\mathrm{OH + ISOP \rightarrow ISOP\text{–}O_2} \tag{1}$$

$$\mathrm{ISOP\text{–}O_2 + NO \rightarrow ISOPONO_2} \tag{2a}$$

$$\mathrm{\rightarrow ISOP\text{–}O + NO_2} \tag{2b}$$

$$\mathrm{ISOP\text{–}O + O_2 \rightarrow MVK(+HCHO) + HO_2} \tag{3a}$$

$$\mathrm{\rightarrow MACR(+HCHO) + HO_2} \tag{3b}$$

$$\mathrm{\rightarrow products + HO_2} \tag{3c}$$

$$\mathrm{HO_2 + NO \rightarrow NO_2 + OH.} \tag{4}$$

Under sunlit conditions the rate of ozone production is equal to the rate of NO oxidation to NO_2, since NO_2 rapidly photolyzes to yield O_3. Thus, the rate of O_3 production from isoprene is equal to the sum of the rates of reactions (2b) and (4), where reaction (4) is meant to indicate only those HO_2 radicals produced as a result of OH reaction with isoprene. If k_2 represents the overall rate constant for the reaction of ISOP–O_2 radicals with NO, then O_3 production from isoprene is expressed as follows:

$$\mathrm{d(O_3\ from\ ISOP)}/\mathrm{d}t = \mathrm{R2b + R4}$$

$$= \mathrm{R1}(k_{2b}/k_2) + \mathrm{R4}. \tag{5}$$

According to the results of experiments conducted by Tuazon and Atkinson (1990), $k_{2b}/k_2 = 0.88$. Thus:

$$\mathrm{d(O_3\ from\ ISOP)}/\mathrm{d}t = \mathrm{R4 + 0.88R1}. \tag{6}$$

In the mechanism above, we have made the reasonable assumption that *all* alkoxy radicals produced as a result of OH reaction with isoprene react (either directly with, or in the presence of O_2) to yield one HO_2 (cf. Atkinson, 1990). In the LFV, where NO concentrations are in the several ppb range, it is also very reasonable to assume that all RO_2 and HO_2 radicals then react with NO (as opposed to reaction with other peroxy radicals), as in reaction (4). Thus, under these conditions,

$$\mathrm{R2b} = \mathrm{R1}(k_{2b}/k_2) = \mathrm{0.88R1} = \mathrm{R4}. \tag{7}$$

Substituting into equation (6) yields

$$\mathrm{d(O_3\ from\ ISOP)}/\mathrm{d}t = 2 \times \mathrm{0.88R1} = \mathrm{1.76R1} \tag{8}$$

i.e. 1.76 molecules of O_3 are formed from each isoprene oxidation by OH. The measured yield for MVK production has been estimated to be 0.35 (Paulson *et al.*, 1992), and thus

$$\mathrm{d(MVK)}/\mathrm{d}t = 0.35 \times \mathrm{R1}. \tag{9}$$

Thus,

$$\frac{\mathrm{d(O_3\ from\ ISOP)}}{\mathrm{d(MVK)}} = \frac{\mathrm{1.76R1}}{\mathrm{0.35R1}} = 5.0. \tag{10}$$

According to this equation, five molecules of ozone are produced for each MVK produced via isoprene oxidation. If we divide this equation by the slope of a regression of the observed (daytime) O_3 vs the simultaneous MVK measurements, we obtain

$$\frac{d(O_3 \text{ from ISOP})/d(\text{MVK})}{d(O_3 \text{ total})/d(\text{MVK})} = \frac{5.0}{d(O_3 \text{ total})/d(\text{MVK})}. \qquad (11)$$

As indicated in equation (11), if we divide 5.0 by the slope of a regression of total $[O_3]$ vs [MVK], we obtain the fraction of the total O_3 production resulting from isoprene oxidation by OH. The principal requirement for such an analysis is that there is fast chemistry, i.e. rapid production of MVK. The slope of the O_3–MVK regression could be increased due to oxidation of MVK by reaction with OH. Thus, this analysis is only valid under conditions where the isoprene oxidation rate is much greater than the MVK oxidation rate, i.e. where $k_1[\text{ISOP}] \gg k_5[\text{MVK}]$, where k_5 refers to the rate constant for the reaction

$$\text{OH} + \text{MVK} \rightarrow \text{products}. \qquad (12)$$

Rearranging, this means that this analysis is valid when $[\text{ISOP}]/[\text{MVK}] \gg k_5/k_1 = 0.18$. This is in fact the case for the daytime period during much of the 1–6 August episode period. For example, for the afternoon maxima (at 1440) on 4 August, $[\text{ISOP}]/[\text{MVK}] = 3.49$, or a factor of 19 greater than the ratio k_5/k_1, for this day representing the extreme in the O_3 and MVK data (which will have the biggest impact on the least-squares slope). Furthermore, as discussed above, MVK is rapidly removed at night in the outflow air, and thus each day the MVK peak is clearly the result of rapid local scale photochemistry. Thus, it appears that equation (11) will hold under the conditions of the 1–6 August episode period.

In Fig. 10 we present a regression of $[O_3 + NO_2]$, i.e. "oxidant", vs MVK, for the daytime only data. The quantity $[O_3 + NO_2]$ is plotted to account for any conversion of O_3 to NO_2 by titration with NO:

$$O_3 + \text{NO} \rightarrow NO_2 + O_2. \qquad (13)$$

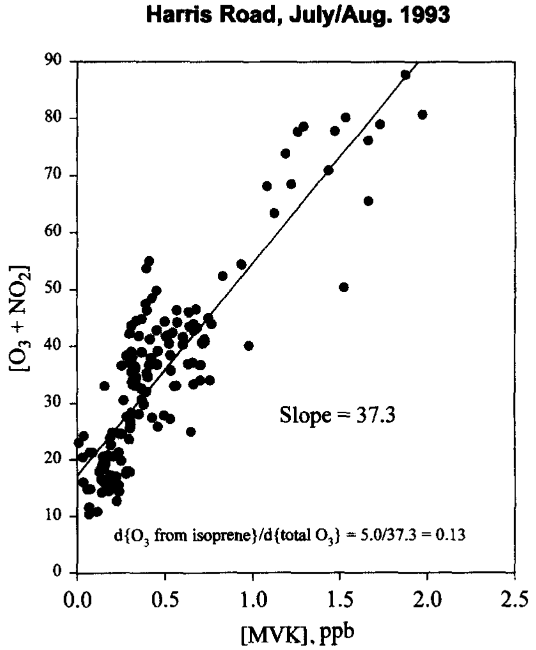

Fig. 10. Regression of "oxidant" vs MVK for daytime data.

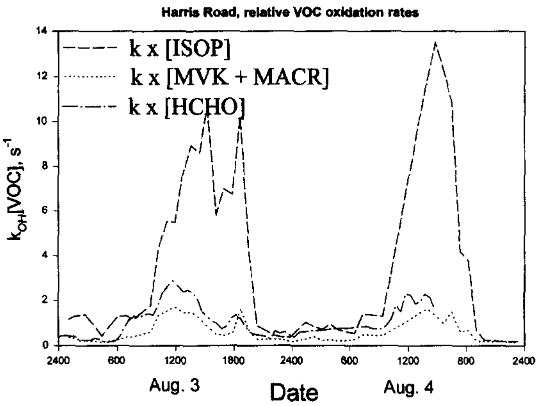

Fig. 11. Plot of the hydrocarbon "reactivity" vs time for 3–4 August.

As shown in Fig. 11, the slope is 37.3. Substitution into equation (11) yields 0.13, i.e. on average, 13% of the ozone production results from OH reaction with isoprene. It should be noted that this is a lower limit in that any destruction of MVK via reaction (12) will increase the slope of the O_3–MVK regression, and thus decrease the calculated fractional contribution to ozone production by isoprene. This is also a lower limit for the contribution of isoprene chemistry to ozone production in that it does not take into account the additional contribution to ozone production by isoprene's oxidation products, MVK, MACR, and HCHO. We should note that this calculation applies only to the conditions measured at Harris Rd, and we know little about the heterogeneity of isoprene and its sources in the LFV. However, MVK will have a lifetime in the LFV of 4 h (assuming $[\text{OH}] = 4 \times 10^6\ \text{cm}^{-3}$) during the daytime. For a wind speed of $5\ \text{m s}^{-1}$, this corresponds to a spatial scale of ≈ 72 km, i.e. over a scale as large as the LFV. Thus, although we are making point measurements, the isoprene product measured is long lived enough that the results likely apply to that for a spatial average across the LFV. This is also likely a good assumption given the turbulent vertical mixing processes that exist during the daytime. That these assumptions are valid is supported by the quality of the MVK–O_3 relationship shown in Fig. 10. Although the finding that isoprene contributes significantly to ozone production in this urban environment is consistent with results for other North American cities, most notably

Atlanta (Chameides *et al.*, 1992), this is the most northerly latitude urban environment where such a result has been obtained.

Measurements in Alabama and Pennsylvania forests (Cantrell *et al.*, 1992; Martin *et al.*, 1991) have indicated that MVK and MACR can contribute significantly to the total hydrocarbon "reactivity", i.e. $\sum_i^n (k_{OH})_i [VOC]_i$. In the LFV this is also the case, although the isoprene products MVK, MACR, and HCHO contribute the most in clean air periods when isoprene is low, and of course O_3 production rates are relatively low. However, depending on time of day, the quantity $\sum_i^n (k_{OH})_i [VOC]_i$ for the isoprene oxidation products can be a significant fraction of the hydrocarbon "relativity" (which is dominated by isoprene in the episode week) even in the episode period, in the early hours of the day. The quantity $(k_{OH})_i [VOC]_i$ for isoprene, (MVK + MACR), and HCHO is plotted in Fig. 11, for 3 and 4 August. It was generally observed that MVK and MACR reached maximum concentrations 2–3 h before isoprene, indicating that the maximum isoprene oxidation rate was similarly several hours earlier than the observed isoprene maximum. These observations are consistent with those of Montzka *et al.* (1993) yet inconsistent with the data of Yokouchi (1994), who found nearly coincident maxima. Early morning photolysis of aldehydes and HONO in an urban environment can serve to shift the isoprene oxidation maxima to earlier in the day and may explain the difference in this case. As shown in the figure, although isoprene dominates the chemistry (among these components), the isoprene products can contribute significantly, depending on time of day. For example, on 3 August, the contribution of the isoprene products relative to the total of (isoprene + its products) was 44% at 1200, but decreased to 16% at the isoprene maximum at 1520.

CONCLUSIONS

The data shown here provide direct evidence for substantial isoprene chemistry occurring in the LFV, through measurements of its atmospheric oxidation products MVK, MACR, and HCHO. Our measurements indicate that isoprene oxidation contributes at least 13% of the total O_3 production rate, during the O_3 episode period. This indicates the importance of inclusion of detailed isoprene chemistry in photochemical models used to investigate O_3 formation in the LFV. However, this will also require improved information regarding fluxes of isoprene from the local vegetation. We have also found that there are significant non-photochemical sources of MVK and MACR, most likely from automotive emissions. It would be useful to make direct measurements of MVK and MACR emission factors (e.g. relative to CO), for appropriate test vehicles, or as part of future tunnel studies.

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