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Analysis of Automated Gas Chromatograph Data from 1996-2001 to Determine VOCs with Largest Ozone Formation Potential

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Introduction

Automated gas chromatograph data collected at TCEQ monitoring sites were analyzed to answer the following questions:

- Which volatile organic compounds (VOCs) are likely to be most important in ozone formation in Houston?
- Does the atmospheric VOC mixture and reactivity vary geographically in the Houston area?
- How often do conditions of high VOC reactivity occur in Houston?

The first question is related to a policy issue. In the original SIP revision proposal of June 2002, twelve compounds and compound groups were listed as candidates for regulation, based upon their reactivities and upon the observations by Brookhaven National Laboratory (BNL) scientists during the TexAQS 2000 study. These twelve compounds and compound groups were ethylene, propylene, all butene isomers, all pentene isomers, 1,3-butadiene, isoprene, all trimethylbenzene isomers, all xylene isomers, toluene, all ethyltoluene isomers, formaldehyde and acetaldehyde. The initial list was developed from the analyses that had been completed at that time. Subsequent analyses, including this analysis, were performed in order to refine the list by using data collected over a longer time period (1996-2001) to assess which compounds contributed most to ozone reactivity.

The second question is closely related to source attribution. TexAQS 2000 data indicated that the reactivity of the VOC mixture emanating from the industrial areas of Houston was often much higher than the urban VOC mixture. This analysis attempted to verify or refute that finding using the multi-year auto-GC data set, and to determine if there were additional geographic variations that might be useful in source attribution.

The third question is directed toward discovering the roles of “routine emissions” and “upsets” in setting the composition of the VOC mixtures observed in Houston. There is much ambiguity in how “routine emissions” and “upsets” are defined, in that “routine” emissions can apparently be continuous or sporadic, and “upsets” can apparently be brief or prolonged. This analysis bypasses the question of defining these terms, and simply asks how often high reactivity is observed. If high reactivity is observed often, then whatever type of release is causing these conditions is not rare.

Methods

Chemistry methods

Automated gas chromatograph (auto-GC) data are available for seven different sites in Houston and vicinity, over varying periods of time.

Site Name	Start date	End date	Number of hours available
Clinton	Aug 20, 1996	Oct 31, 2001	26,868
Deer Park	Jan 16, 1997	Oct 31, 2001	17,547
HRM 7	Aug 27, 2001	Oct 31, 2001	1375
HRM 3	Aug 21, 2001	Oct 31, 2001	1505
Channelview	Aug 4, 2001	Oct 31, 2001	1195
Aldine	Aug 31, 2000	July 30, 2001	3034
Bayland Park	May 4, 1998	Aug 7, 2000	5783

The auto-GCs were operated according to EPA PAMS site guidelines and TNRCC guidelines. The auto-GC data and meteorological data were validated by TNRCC staff. Additional QA and peer review was performed by Sonoma Technology; more detail is available from Main et al., 2002.

Reactivity scales

The purpose of this analysis was to determine which compounds have the greatest potential to cause rapid ozone formation. Ozone formation potential is measured in this analysis by two using two reactivity scales: the OH reactivity, i.e., the product of the reaction rate constant of the OH radical $k(\text{OH})$ and the concentration of the compound, and the maximum incremental reactivity (Carter, 1994), i.e., the maximum amount of ozone created by the incremental addition of a particular VOC.

OH reactivity

OH reactivity is a measure of how rapidly a compound begins participating in ozone formation. Although there are other chemical pathways as well, the speed at which a compound reacts with OH is one of the major factors in determining how aggressively the compound enters the ozone formation process. Other reactivity measures, such as Maximum Incremental Reactivity (MIR), measure the total ozone formation potential under optimal conditions over the lifetime of the compound and its reaction products. MIR reactivity, therefore, may manifest itself over a longer period of time than 1-3 hours. The observations of rapid ozone in Houston are consistent, however, with ozone formation and accumulation over 1-3 hours or less. Therefore, OH reactivity may be a better measure of the potential of a VOC to cause rapid ozone formation. However, it should be noted that at very high OH

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reactivity values, VOCs can react with radicals at such a high rate that they quench the formation of ozone by aggressively competing for radicals with the nitrogen species.

The OH kinetic reaction coefficients ($k(\text{OH})$) used in this study for each compound are presented in Appendix A. OH reaction coefficients for each compound were obtained from Roger Atkinson at UC-Riverside (Atkinson, personal communication, 2002). For co-eluting compounds, the $k(\text{OH})$ for the slowest compound was used. Note that this analysis uses OH reaction constants at standard temperature (298 K) and standard pressure (1 atm), not actual temperature or actual pressure. The reason for using standard temperature is to ensure that the differences seen in reactivities are due solely to $k(\text{OH})$ and concentration. Later analyses may investigate how sensitive the OH reactivities are to actual temperatures measured concurrently with the VOC measurements.

The OH reactivity for each compound is calculated by multiplying the $k(\text{OH})$ rate constant by the respective compound concentration in ppbv. Most of the time, no OH radical concentration data are available. Therefore, OH radical concentration is not included in the OH reactivity metric described in this analysis. The true reaction rate, of course, depends strongly upon OH concentration, but this analysis focuses more on the relative importance of different VOCs rather than calculation of actual concentrations. Essentially, this analysis describes the relative importance of different VOCs, assuming all other factors (OH concentration, temperature, etc.) are equal.

Maximum Incremental Reactivity (MIR)

The second reactivity scale used in this analysis is MIR reactivity. The OH scale does not account for the ozone formation reactions that occur after the initial VOC-OH reaction; the MIR scale does. The MIR reactivity is based upon research by Carter and others at UC-Riverside, who sought a method of quantifying the reactivity differences among VOCs that were observed in chamber studies (Carter, 1990; Carter, 1995; Carter et al., 1995). One of the metrics they developed, MIR, represents the maximum incremental formation of ozone due to adding a small amount of additional VOC to a chamber that had optimum conditions for the formation of additional ozone. The MIR scale follows the reaction path of the VOC and its subsequent reaction products to determine the resultant ozone formation from the original VOC addition to a closed system. These reactions can evolve over longer periods of time than the initial OH reaction. It has been used in a number of studies to assess the reactivity of urban VOC mixtures, and to contrast the reactivity between cities. This measure has been commonly used in studies throughout the country.

Appendix B includes the MIR values for the auto-GC compounds as of 13 November 2000, obtained from Dr. Carter's website (<ftp://ftp.cert.ucr.edu/pub/carter/SAPRC99/r99tab.xls>). Hourly MIR reactivity for each compound was calculated by multiplying the concentration of VOC in ppbv by the MIR constant, and by the ratio of the molecular weights of the VOC of interest and ozone. The calculations again assumed standard temperature and pressure. For co-eluting compounds, the lowest MIR value was used to calculate the MIR reactivity for the compounds.

Description of the data used

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Related compounds were grouped together in order to reduce the number of categories on the graphs. Table 2 shows the key to the group names. Each colored band or pie slice within the figures below represents the reactivity contributed by a single group of compounds.

In some of the following analyses, all auto-GC data available were included. In other analyses, the reactivity data were filtered in several ways to select out the observations of greatest interest. The paragraphs below describe how the data were filtered to obtain a dataset containing only the samples with highest total reactivity for each day at each site.

First, only data with the sum of all compounds greater than 100 ppbC were selected, to avoid some problems associated with approaching the minimum detection limits.

Only data from “ozone season” months were included. Although high ozone can occur in Houston during almost any month of the year, we selected data from June-October for this analysis, since high ozone occurs most often and most severely during these months.

The data were filtered further to select out only those observations that had high total reactivity. Total reactivity is the sum of the individual reactivities of all the species measured. The high reactivity threshold is based upon the 90th percentile of observed total reactivity for the airborne canisters taken during TexAQS 2000. BNL observed only 25 canister samples with reactivity greater than 10/sec, out of a total of 232 observed, only 10.8% of the total. When all canisters from all aircraft flown during 2000 and 2001 are considered, the 90th percentile total OH reactivity is 9.1/sec. For convenience, the “high” total reactivity threshold will be set at 10/sec for this analysis. Likewise, the 90th percentile total canister MIR reactivity for all airborne canisters taken in 2000 and 2001 is 166, so this value will be used as the high MIR reactivity threshold. It is appropriate to use the airborne canister data to set the definition of high reactivity because the aircraft samples were taken throughout the eight-county ozone nonattainment area, whereas auto-GCs are stationary and can only sample at a particular location, which may not be representative of the entire domain.

Group name	PAMS Compounds included
ethylene	ethylene
propylene	propylene
butenes	1-butene, cis-2-butene, trans-2-butene
pentenes	1-pentene, cis-2-pentene, trans-2-pentene, 2-methyl-2-butene, 3-methyl-1-butene
xylenes	ortho-xylene, meta- and para-xylene (the latter two co-elute)
ethyltoluenes	ortho-, meta-, and para-ethyltoluene
trimethylbenzenes	1,2,3-trimethylbenzene; 1,2,4-trimethylbenzene; 1,3,5-trimethylbenzene
butanes	n-butane, isobutane
C2C3	ethane, propane, acetylene

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butadiene	1,3-butadiene
isoprene	isoprene
alkanes	C5: isopentane; n-pentane C6: n-hexane; 2,2-dimethylbutane; 2,3-dimethylbutane; 3-methylpentane; 2-methylpentane C7: n-heptane; 2,4-dimethylpentane; 2,3-dimethylpentane; 2-methylhexane; 3-methylhexane C8: n-octane; 2,2,4-trimethylpentane; 2,3,4-trimethylpentane; 2-methylheptane; 3-methylheptane C9: n-nonane C10: n-decane
cycloalkanes	cyclopentane, cyclopentene, methylcyclopentane, cyclohexane, methylcyclohexane,
aromatics	benzene, ethylbenzene, isopropylbenzene, n-propylbenzene, meta-diethylbenzene, para-diethylbenzene

Only data from “daytime” hours were included. These data were divided into two groups: morning transition (defined as 5 am local standard time(LST) to 8 am LST), and midday (9 am to 3 pm LST). These two time periods were studied first since it is more likely that ozone forming in the afternoon will be influenced by morning and midday concentrations than by concentrations observed later in the day.

Within the midday and morning transition periods, the 1-hour observation with the highest total reactivity was selected for each day. In this manner, the total number of days with high reactivity could be determined. This is analogous to the ozone standard, in that the total number of exceedance days is the important quantity, not the total number of exceedance hours.

One would expect midday summer reactivities to be the lowest observed, for two reasons. First, the greater photochemical activity during summer days will deplete the concentrations of the most highly reactive compounds. Second, midday summer planetary boundary layer heights are greater than any other time of year. The increased height of the boundary layer allows emissions to disperse into a greater volume, thus reducing their concentrations. So this analysis does not exaggerate the reactivities; on the contrary, it presents the data that is potentially the lowest in reactivity. Therefore, conclusions that can be reached about total reactivity from this data set will, by nature, be conservative.

Results

Frequency of high reactivity

Table 3 shows how often high reactivity occurred at least once per day during the midday hours during ozone season.

Table 3. Frequency of high reactivity days during midday hours of ozone season. High reactivity is defined as total OH reactivity > 10; total MIR reactivity > 166.					
Site	No. of days with high OH reactivity	% days with high OH reactivity	No. days with high MIR reactivity	% days with high OH reactivity	Total number of ozone season days sampled
Aldine	11	9%	10	8%	122
Bayland Park	23	6%	27	7%	374
Channelview	37	42%	37	42%	88
Clinton	493	59%	483	58%	837
Deer Park	254	33%	255	33%	765
HRM 3	47	64%	46	64%	73
HRM 7	42	59%	43	58%	67

Clinton, HRM 7 and HRM 3 sites observed high reactivity on about 60% of the measurement days; Deer Park and Channelview observed high reactivity about 30-40% of the time during midday hours. The implication is that high reactivity days are fairly commonplace, and do not represent unusual conditions, except at the Aldine and Bayland Park sites, which are well removed from the industrial areas. The more typical urban emissions that surround the Aldine and Bayland Park monitors cause high reactivity during midday less than 10% of the time.

A second point is that high reactivity occurs at some sites more often than high ozone occurs in the monitoring network. The auto-GC study by Main et al., 2002 found that there was no statistical difference between the observed MIR reactivity on ozone episode days and non-episode days. These results could imply that high VOC reactivity is not the only factor that affects ozone formation. Meteorological conditions that allow stagnation, strong sunlight, and mixing with NO_x emissions are known to be important factors in high ozone episodes in Houston, so it is likely that meteorology determines whether high reactivity plumes react to become high ozone plumes. It should be noted, however, that the ozone monitoring network missed a number of large ozone exceedances during TexAQS 2000, so that the lack of correlation between high reactivity and high ozone may be due in part to the inadequacies of the network.

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A third point of interest is that Table 3 shows the OH and MIR reactivity scales measure high total reactivity almost exactly the same number of days.

Morning transition hours are more likely to have high reactivity than midday hours at all sites, though at some sites the effect is large and at others it is small. Table 4 shows percentage of hours with high ozone for midday hours and morning transition hours. Note that Table 4 refers to *hours*; Table 3 refers to *days*. Channelview shows the greatest difference between midday and morning transition: high reactivity is observed 64% of the time during morning transition, but only 30% of the time during midday hours. At HRM 7, however, the percentage of high reactivity hours is nearly the same for midday (57%) and morning transition (60%).

Site	Midday hours			Morning transition hours		
	Hours with OH reactivity > 10/sec	Total hours with valid observations	% hours > 10/sec	Hours with OH reactivity > 10/sec	Total hours with valid observations	% hours > 10/sec
Aldine	13	163	8.0 %	123	272	45.2 %
Bayland Park	37	327	11.3 %	223	728	30.6 %
Channelview	81	272	29.8 %	158	248	63.7 %
Clinton	1556	3311	47.0 %	1525	2520	60.5 %
Deer Park	596	1783	33.4 %	972	2003	48.5 %
HRM 7	141	249	56.6 %	126	211	59.7 %
HRM 3	170	286	59.4 %	175	234	74.8 %

Relative importance of VOCs

Figures 1-7 show the relative importance of different groups of VOCs measured by the auto-GCs. Each pie slice represents the median MIR reactivity of each compound group relative to the sum of median reactivities of all groups. These figures display all available data at each site, not just the 90th percentile of total reactivity.

At all sites, ethylene and propylene are of primary importance, but there are differences among the other compound groups at each site. Alkanes make an important contribution at all sites, but note that the alkanes group represents 19 compounds, whereas the other groups generally represent 3-5 compounds. Deer Park is dominated by only ethylene and propylene; Clinton shows significant contributions by several additional compound groups, including butenes, pentenes, butanes, and

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xylenes. HRM 7 shows a large contribution from 1,3-butadiene as well as ethylene and propylene. HRM 3 shows a large contribution from butenes and xylenes as well as ethylene and propylene. Channelview is dominated by ethylene and propylene, but butanes also play a large role. The “urban” sites, Aldine and Bayland Park, also have large contributions to total reactivity by ethylene and propylene, and other groups that contribute include butenes, butanes, and xylenes. In fact, the Clinton site and the Aldine and Bayland Park sites display very similar patterns when all hours of available data are considered.

Figures 8-14 show similar pie charts that include only the high reactivity samples (i.e., those with total MIR reactivity > 166). Each pie slice represents the mean MIR reactivity of each compound group relative to the sum of the mean reactivities of all groups. While these charts show similar patterns as Figures 1-7, some highly reactive species clearly have enhanced reactivity on the highly reactive days. For example, on high reactivity days at Deer Park and Channelview, ethylene and propylene account for 60-70% of the total MIR reactivity. HRM 7 shows a large contribution from 1,3-butadiene, on average accounting for 14% of the total MIR reactivity, which is greater than the average contribution by ethylene. At Clinton, the single largest compound group is butanes, which account for 19% of the total MIR reactivity, and four other compound groups—ethylene, propylene, butenes, and alkanes—account nearly equal amounts of reactivity. At HRM 3, butenes and ethylene account for the same percentage of reactivity—16%. Aldine and Bayland Park both seem to show high ethylene and propylene contributions for the few samples with total MIR reactivity > 166.

The differences between the high reactivity case (only days with total MIR > 166) and the general case (all available data) suggest that high reactivity in some cases seems to be associated with certain groups of compounds which appear in larger concentrations on high reactivity days. High reactivity days do not necessarily have more of all compounds; rather they have relatively more of selected compounds. These selected compounds vary from site to site: Clinton has relatively more butanes; Deer Park, Channelview, Bayland Park and Aldine have relatively more ethylene and propylene; HRM 3 has relatively more butenes; HRM 7 has relatively more butadiene and propylene.

Reactivity analyses using the MIR scale

The next series of figures present the distribution of reactivity by compound group for all days with maximum hourly total reactivity greater than the 90th percentile of the TexAQS 2000 airborne canisters. For the MIR scale, all days with at least one hour with total MIR reactivity greater than 166 have been represented; for the OH scale, the high reactivity threshold is 10. Each of these high reactivity days are represented by the sample with the highest total reactivity measured on that day.

In each graph, the days have been ranked by total reactivity. These graphs allow the reader to compare the total MIR reactivity among sites, as well as to compare the distribution of reactivity among samples at the same site and at different sites.

Figures 15-17 show midday summer MIR reactivities for the Clinton site. Figure 15 shows all samples with MIR > 166; figure 16 shows only the top 50 days so that the details of individual samples can be seen. These data reflect the finding mentioned above—that high reactivity days at

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Clinton seems to be dominated by butanes, which is unique among the 7 auto-GC sites. Figure 17 shows what the total MIR reactivity measured by the auto-GC would be if all olefins were removed from the atmosphere. The total reactivity is still very high at Clinton, indicating that light olefins are not the only important cause of high reactivity. Because butanes have relatively low MIR values, they must be present in extremely high concentrations to achieve such high reactivities. Butanes have occasionally been measured at Clinton in excess of 10,000 ppbC.

By contrast, figure 18 shows Deer Park, where ethylene and propylene dominate the reactivity. If all light olefins were removed from these samples, the reactivity would clearly be very low. Figure 19 shows HRM 3, where butenes dominate the reactivity on the highest reactivity days, though ethylene and propylene dominate much of the time. On three days, pentenes dominate the reactivity, and on four days, 1,3-butadiene dominates. Figure 20 shows HRM 7, where 1,3-butadiene is observed to dominate the reactivity often, sometimes in concert with pentenes. Figure 21 shows Channelview, which is similar to Deer Park in that it is usually dominated by ethylene and propylene. Figures 20 and 21 show Aldine and Bayland Park, respectively. These two sites observe high reactivity days much less often than the industrial sites, and the maximum reactivities are generally lower. Isoprene dominates the reactivity at these urban sites occasionally, due in part to the lower total reactivity observed at these sites. The isoprene is probably of biogenic origin at these sites.

On some of these figures, there seem to be recurring patterns of colors that may represent a characteristic emission signature from a specific type of facility. These patterns may be useful in source apportionment studies which will be conducted later.

Reactivity analyses using the OH reactivity scale

Figures 24-28 display similar reactivity information using the OH reactivity scale. While there are noticeable differences from the MIR figures, in general the OH reactivity scale leads to the same conclusions as the MIR scale: the consistent importance of ethylene and propylene, the importance of butenes and 1,3-butadiene at HRM 3 and HRM 7, the importance of butanes at Clinton.

Table 5 shows the mean percentage of total OH reactivity accounted for by olefins at each site. At most sites, total OH reactivities drop well below 20/sec when all olefins are removed. But at Clinton, there are still 24 days with total reactivity > 20/sec even when the olefin contribution is removed. On most of these days, butanes are responsible for the high reactivity. The other alkanes sometimes play a significant role in the high reactivity as well. On one day, the Clinton site observed over 60/sec of reactivity due solely to xylenes. Xylenes' reactivity did not exceed 20/sec on any other day or at any other site.

Site	Mean % reactivity due to olefins	Mean total OH reactivity with olefins (1/sec)	Mean total OH reactivity without olefins
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			(1/sec)
Clinton	55	26.6	11.3
Deer Park	76	25.3	4.6
HRM7	72	30.6	7.1
HRM3	68	25.3	7.3
Channelview	68	22.2	6.4
Aldine	55	13.9	6.2
Bayland Park	60	16.6	6.5

Hexenes were not quantified at most sites, but were sporadically quantified at Clinton. In the calculations made here, they are not included in the olefin category, because we usually have no data for them. On one day for which they were quantified at Clinton, however, hexenes' reactivity reached 16/sec, indicating that they may play an important role, but more data are needed to firmly establish this assertion.

Isoprene, a highly reactive compound emitted by some species of trees, plays a significant role in high reactivity days only at non-industrial sites (Aldine and Bayland Park). It does not exhibit behavior consistent with any significant industrial sources, at least for this midday summer data set. If high concentrations of isoprene were to be observed during the winter and/or at night, especially as a sharp spike, then an industrial source would be more likely. But the analyses necessary to find such observations have not yet been completed.

Reactivity during morning transition hours

Morning transition hours shows a similar pattern to the midday hours, with a few exceptions. Figure 29 shows the HRM 3 OH reactivities for days with total OH reactivity > 10. The OH reactivities during morning transition hours tend to reach higher values than during midday. At Deer Park, the highest reactivity observed was over 500/sec, and more than 30 days had reactivities greater than 100/sec. During morning transition hours, the alkanes group plays a larger role at Clinton and Deer Park. Alkanes, cycloalkanes, butanes, and on one occasion, styrene play a larger role during morning transition hours than midday hours at Deer Park. At HRM 7, cyclic compounds seem to play a significant role on several days, perhaps due to the influence of cyclopentene. At Channelview, a mixture of butanes, other alkanes, and even C2C3 compounds (propane, ethane, acetylene) seem to play a significant role on a few days. At Aldine, the highest reactivity observed (77/ sec) was primarily due to isoprene. Analyses of morning transition, evening transition, and nighttime hours is incomplete; these analyses will be available for the mid-course review.

Other reactivity scales compared to MIR

Other reactivity scales could be used to evaluate relative reactivities in Houston, and some of these may be more appropriate than the MIR scale. The different scales are based upon the assumed environment into which a given VOC is released. If conditions are suitable for maximum formation of ozone given a small increase in VOC_i, then the relative reactivities of compounds are well-

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described by the MIR scale. If conditions are suitable, however, for achieving maximum peak ozone concentration with addition of VOC_i , the MOIR is most suitable. Finally, if conditions are such that the system is equally sensitive to NOX and VOC_i , then the EBIR scale is most appropriate. Researchers at UT have indicated that their box modeling and chamber studies point to the EBIR scale as the most appropriate for Houston (Allen, personal communication, 2002). Others have suggested that MOIR may be most appropriate (Jeffries, personal communication, 2002). However, Figure 31 shows that use of other reactivity scales is unlikely to change the relative importance of compounds as calculated by the MIR scale. The reactivities of the twelve HRVOCs of interest were calculated relative to the reactivity of propene for each of the three scales. Then the ratios for the MOIR and EBIR scales were plotted versus the MIR ratios. The absolute values of the reactivities are highest for the MIR scale, and no compounds were found to be less reactive relative to propene on the MIR scale and more reactive relative to propene on another scale. This suggests that the findings are somewhat robust; regardless of which scale is used, the light olefins usually dominate the reactivity, and other compounds dominate the reactivity occasionally.

Reactivity analysis of TexAQS 2000 canisters

Figures 32 and 33 show the distribution of OH reactivity for airborne canister samples collected by BNL and NCAR/NOAA scientists, respectively. These data were collected during August and September 2000. They are presented here to show that total OH reactivity during the TexAQS 2000 field study period was not unusually high. Many auto-GC samples show much higher total OH reactivity than the highest reactivity airborne canisters. For example, a sample collected at the Deer Park auto-GC on October 4, 1999 during the morning transition hours had a total OH reactivity of 548/sec—this sample's reactivity was dominated by ethylene and propylene, which is consistent with the VOC mixture usually observed at Deer Park.

The composition of the BNL samples, however, was somewhat unusual. Figure 32 shows that toluene was seen in large quantities, as well as some compounds not measured by the auto-GCs. At the auto-GC sites, high toluene reactivity is somewhat unusual. Analyses of these samples are ongoing, using trajectories and other tools that may allow proper source apportionment. Further discussion of the airborne canister data can be found in Boyer et al., 2002.

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Conclusions

Analysis of automated gas chromatography data collected in Houston between 1996-2001 has provided some answers to the questions posed in the introduction.

Which VOCs are likely to be most important in ozone formation in Houston?

These compounds were *frequently* responsible for high reactivity days: propylene, ethylene, butenes (1-butene, c-2-butene, t-2-butene), and 1,3-butadiene.

A second group of highly reactive compounds exhibited very high reactivity *occasionally*: pentenes, xylenes, and hexenes.

A third group of compounds, n-butane and isobutane, are normally low reactivity compounds, but have been detected in such extremely high concentrations that they are responsible for very high reactivity.

Several compounds identified earlier as candidates for regulation have not been detected at high reactivities during summertime midday conditions by the auto-GCs: toluene, ethyltoluenes, and trimethylbenzenes. However, toluene and trimethylbenzenes caused high reactivity in several TexAQS 2000 airborne canister samples. Styrene, which was considered for the list of candidate compounds, has not been seen at high reactivities in midday summer samples.

Many compounds that may contribute to high reactivity are not measured by the auto-GCs. Two compounds that are known to play an important role in ozone formation, formaldehyde and acetaldehyde, are not measured by the auto-GCs, but are measured using other techniques routinely by TCEQ. These carbonyl data will be analyzed later. Analyses of BNL, NOAA, NCAR, Baylor/EPA, event-triggered canisters, HRM network canisters, TCEQ toxics monitoring, and other data sets may reveal other compounds that play a large role in reactivity.

Does the atmospheric VOC mixture and reactivity vary geographically in the Houston area?

Auto-GCs have sampled at seven locations in Houston, and the composition of the VOC mixture observed at these different sites varies substantially. At most sites, ethylene and propylene are the dominant contributors to reactivity, but the secondary contributors vary from site to site. Composition of the VOC mixture at Bayland Park and Aldine, the two sites influenced most by urban emissions rather than industrial emissions, have very similar compositions. Composition at the industrial sites of Channelview, Clinton, Deer Park, HRM 3 and HRM 7, however, vary substantially, probably due to the type of industries in the vicinity of the monitoring sites. Additional monitoring data at many different sites in the industrial area are essential to determining the overall variability of VOC mixture so that all compounds responsible for high reactivity can be identified.

How often do conditions of high VOC reactivity occur in Houston?

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At three auto-GC sites in close proximity to industry, high reactivity occurs 50-60% of the time; at two others, high reactivity occurs 30-40% of the time. At two auto-GC sites well removed from the industrial complex, high reactivity occurs less than 10% of the time. The frequent occurrence of high reactivity suggests that regardless of whether emission events are defined as “routine” or “upsets”, they seem to occur more than half the time in the industrial areas.

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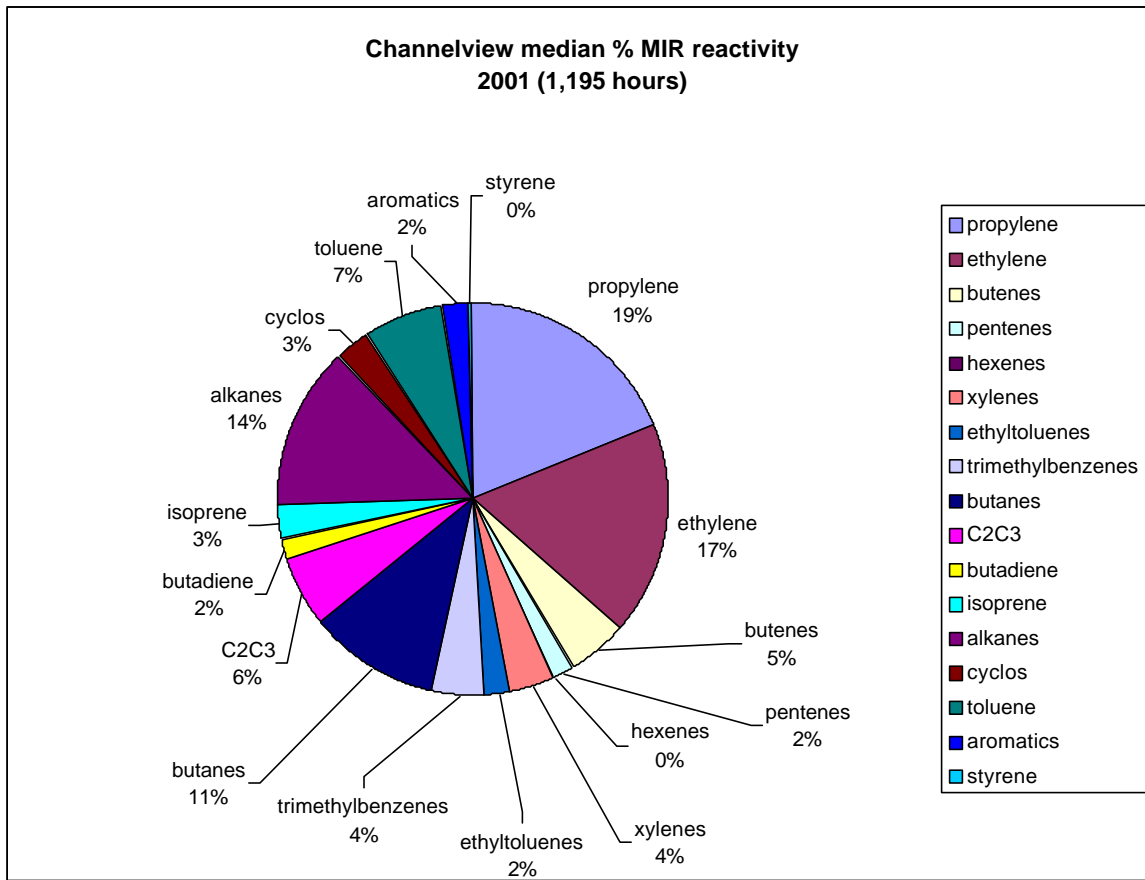


Figure 1. Channelview MIR reactivity of compound groups, all available data.

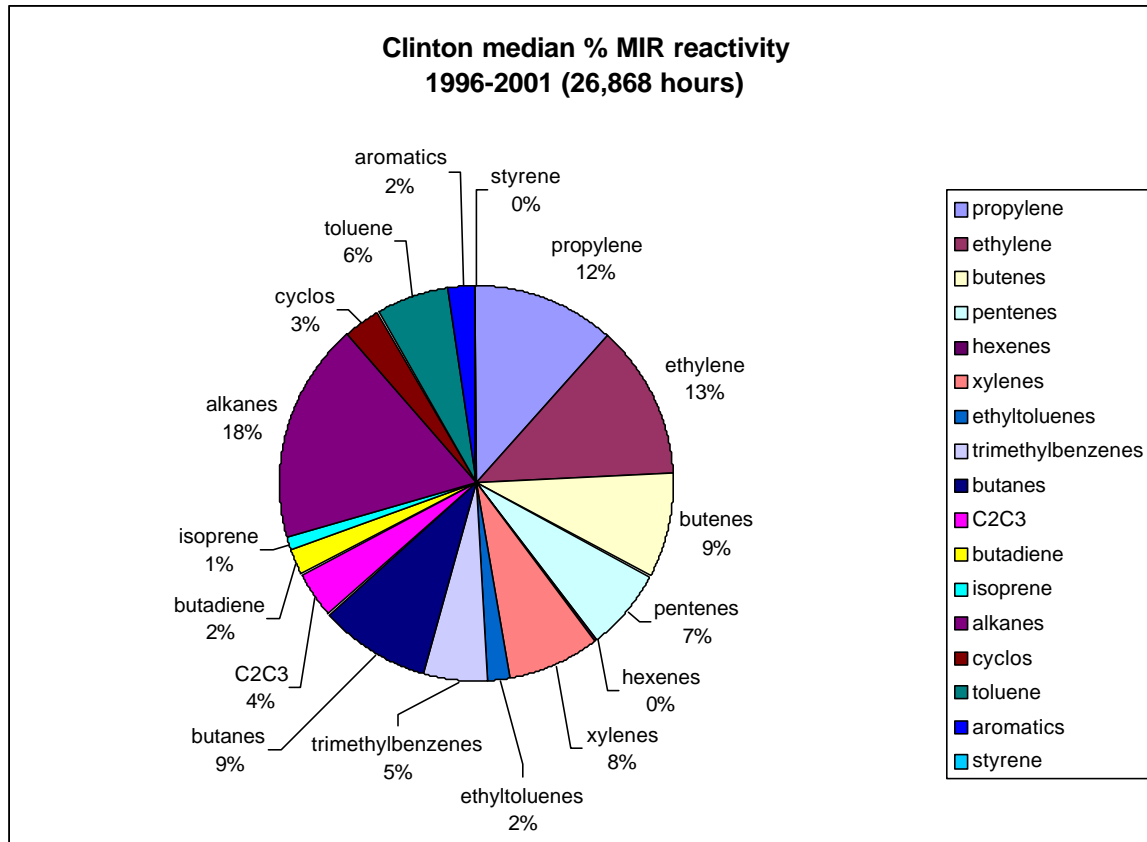


Figure 2. Clinton MIR reactivity of all compound groups, all available data.

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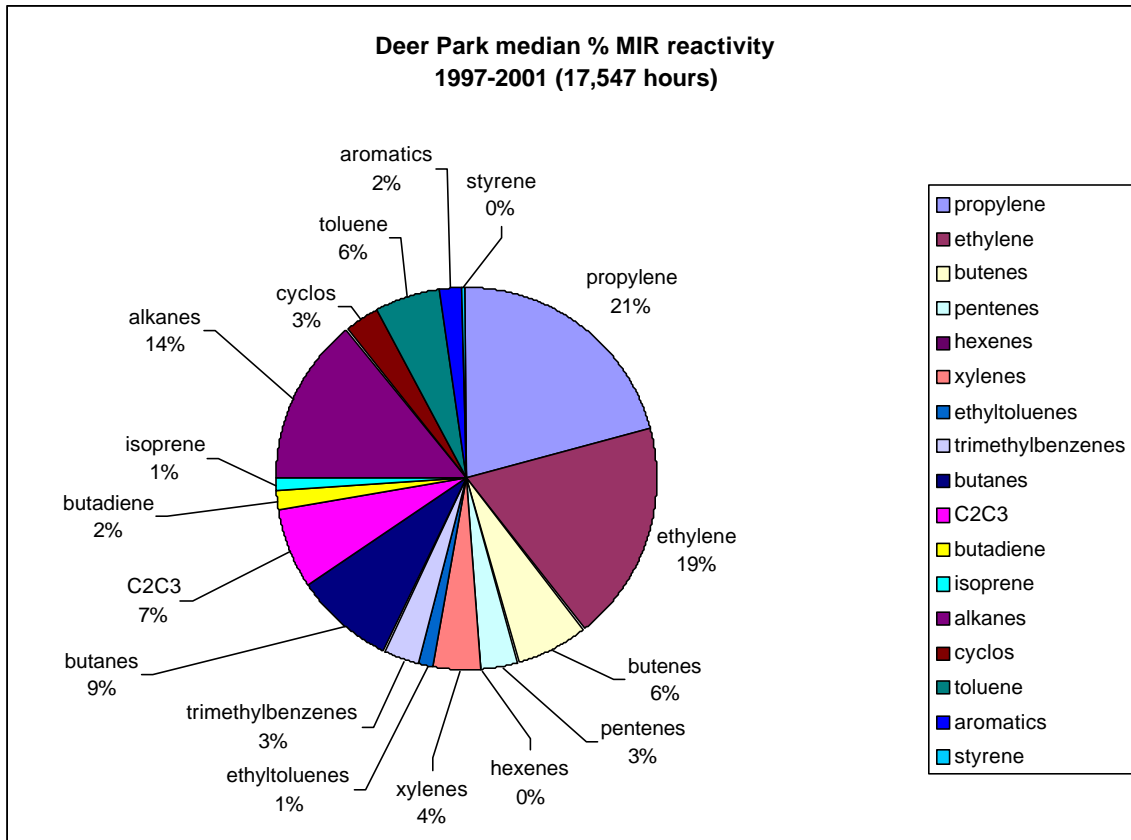


Figure 3. Deer Park MIR reactivity for all compound groups, all available data.

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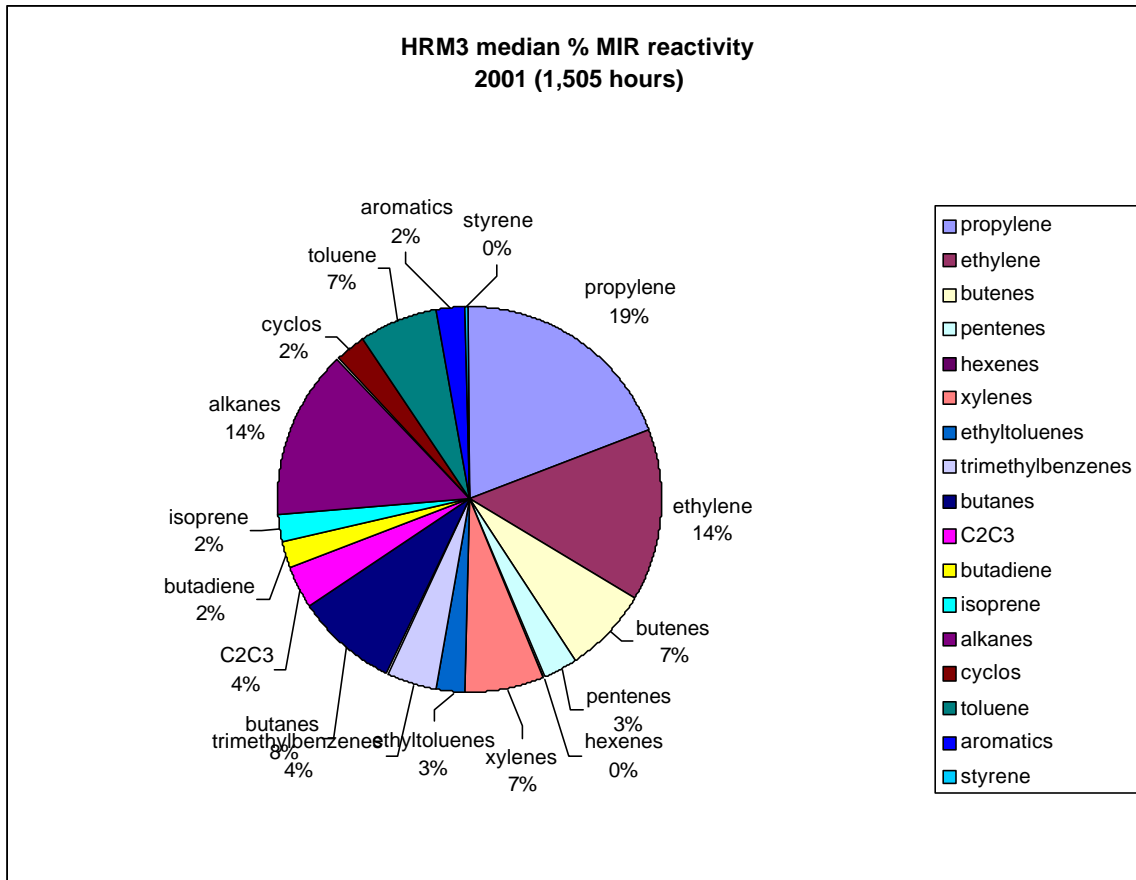


Figure 4. HRM 3 MIR reactivity for all compound groups, all available data.

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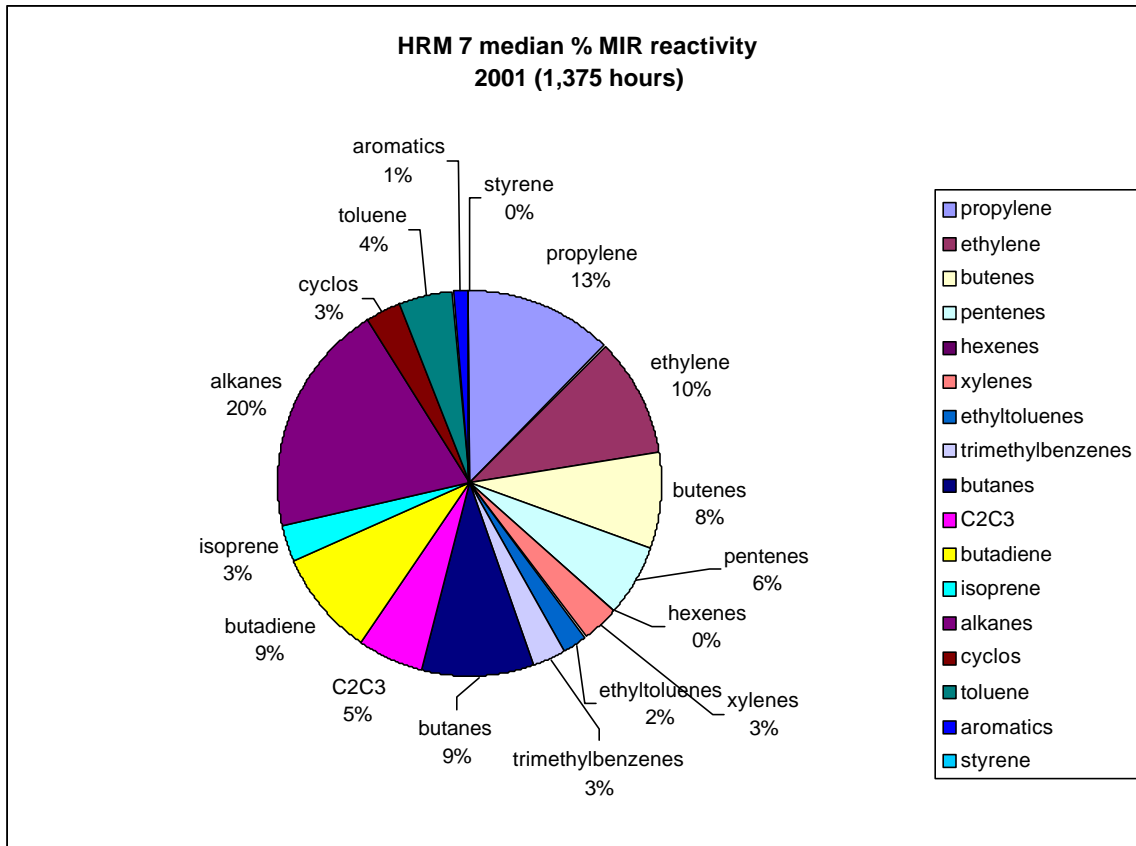


Figure 5. HRM 7 MIR reactivity for all compound groups, all available data.

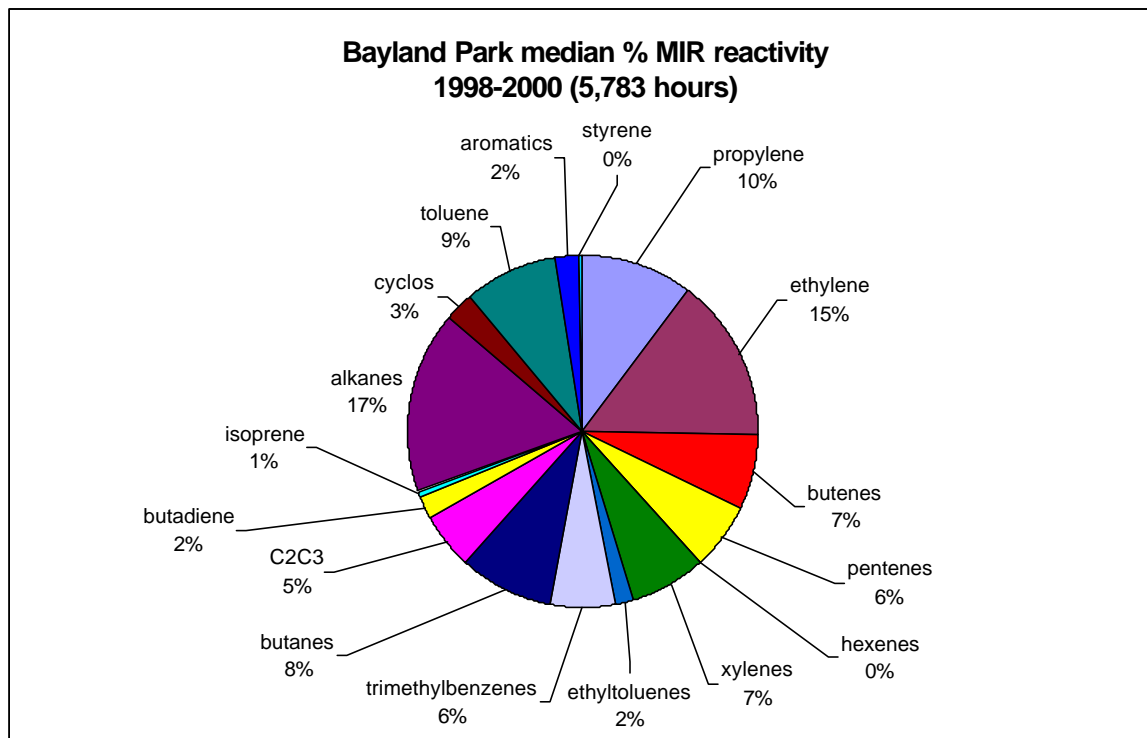


Figure 6. Bayland Park MIR reactivity for all compound groups, all available data.

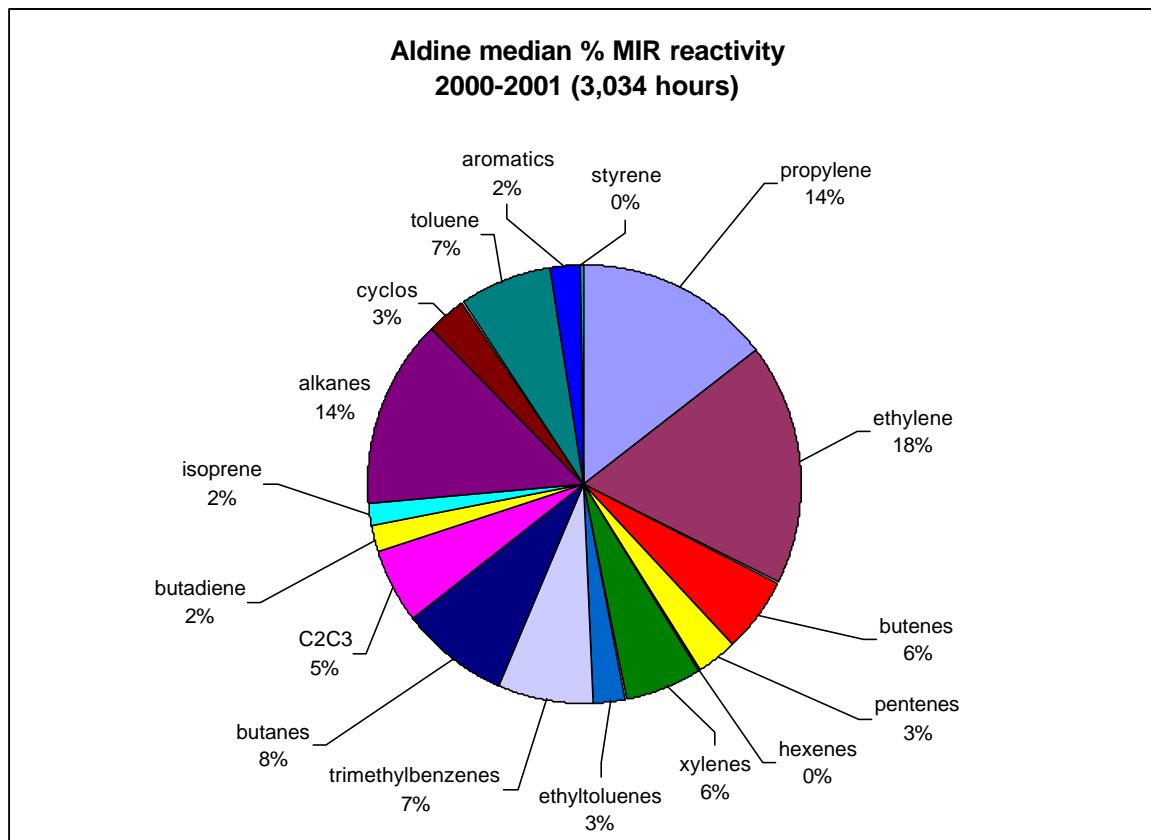


Figure 7. Aldine MIR reactivity for all compound groups, all available data.

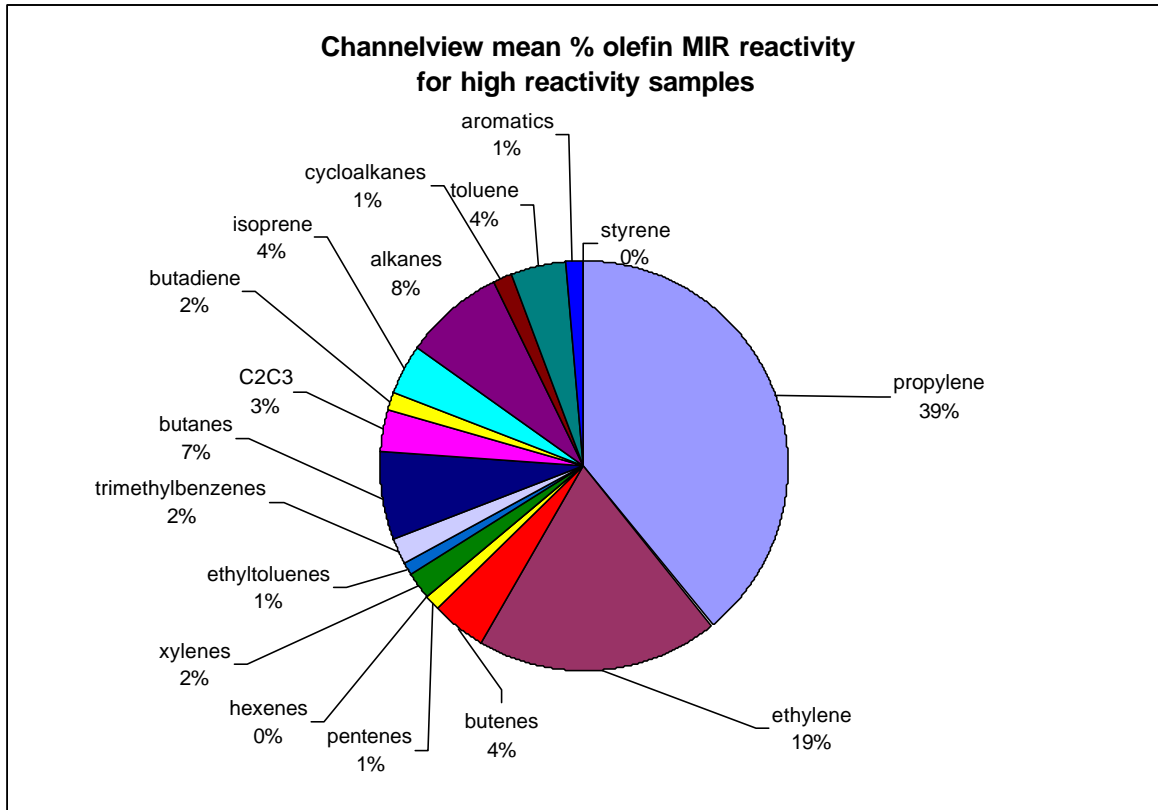


Figure 8. Channelview MIR reactivity for samples with total MIR reactivity > 166.

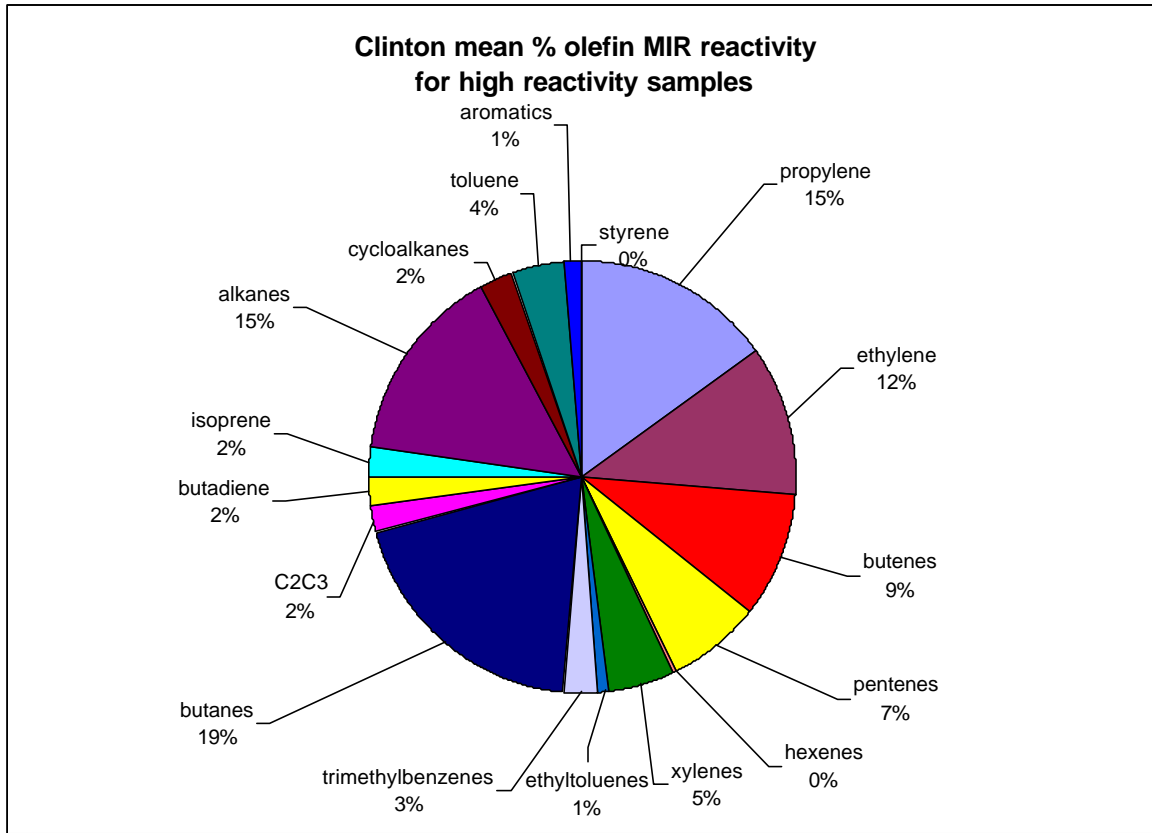


Figure 9. Clinton MIR reactivity for samples with total MIR reactivity > 166.

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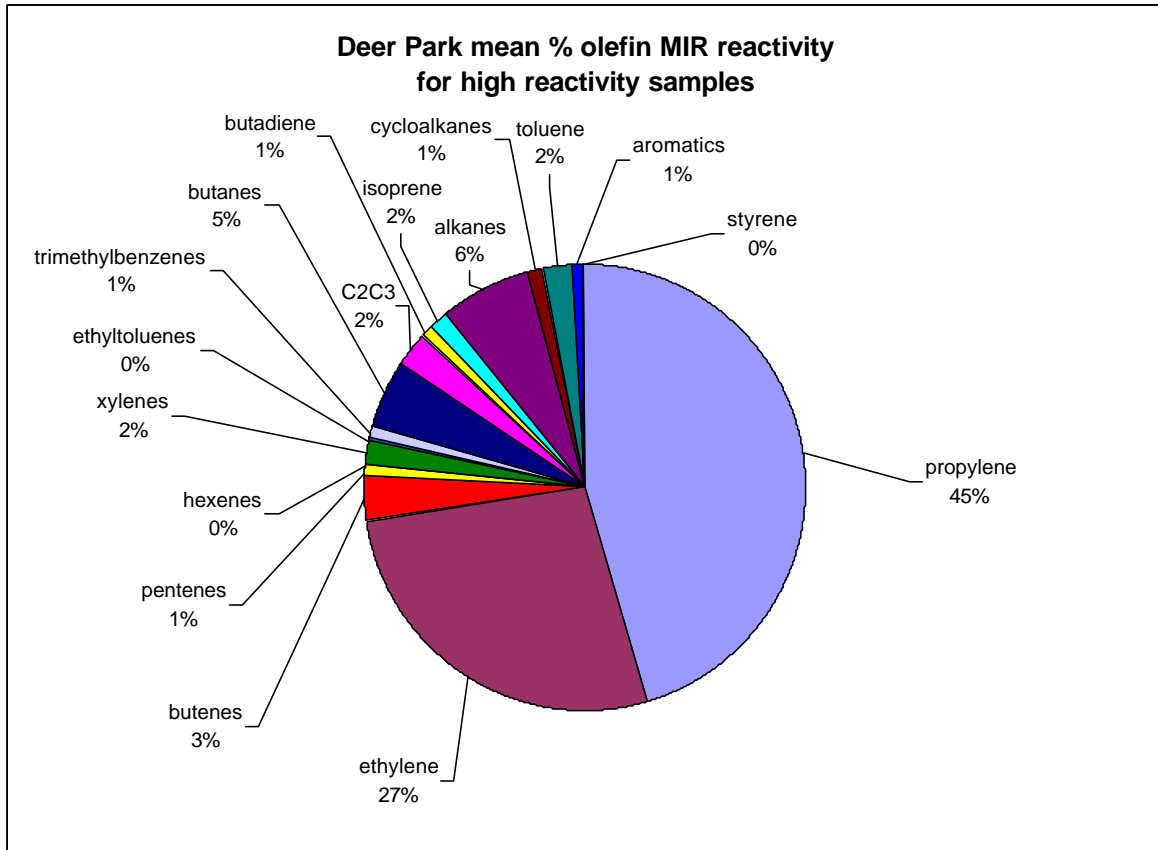


Figure 10. Deer Park MIR reactivity for samples with total MIR reactivity > 166.

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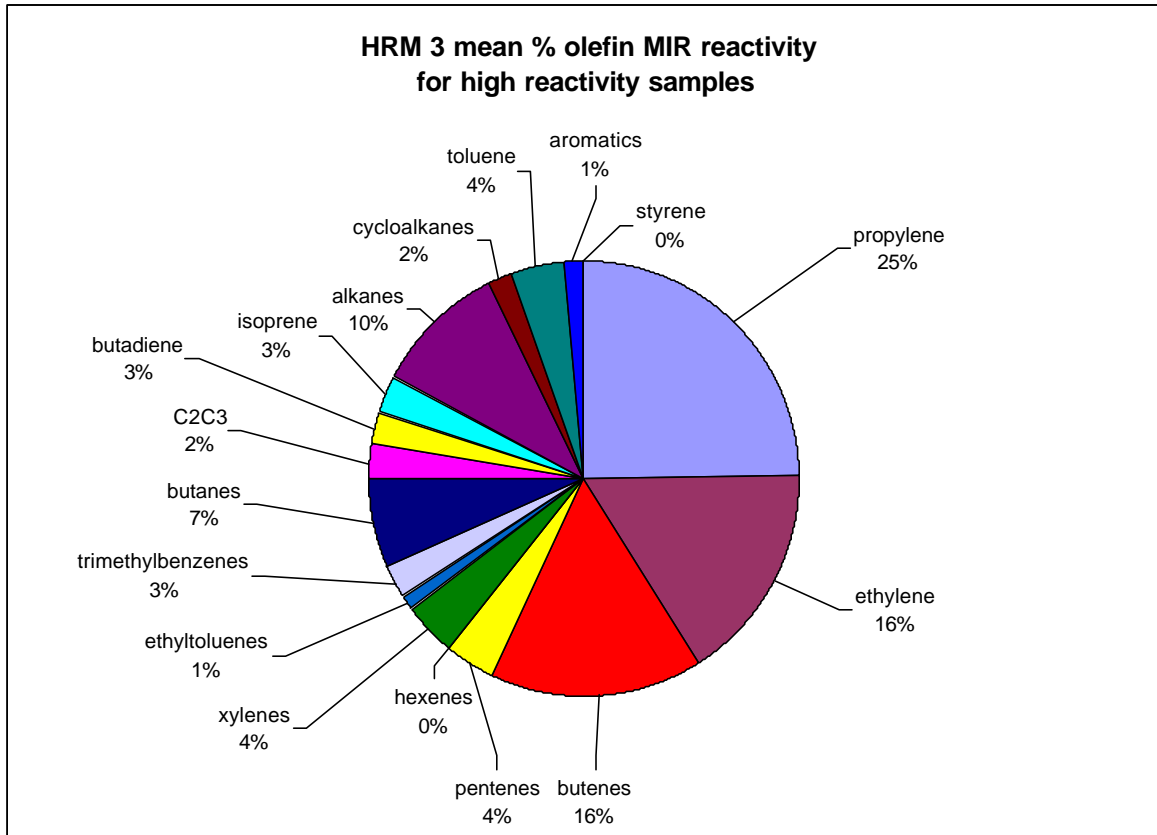


Figure 11. HRM 3 MIR reactivity for samples with total MIR reactivity > 166.

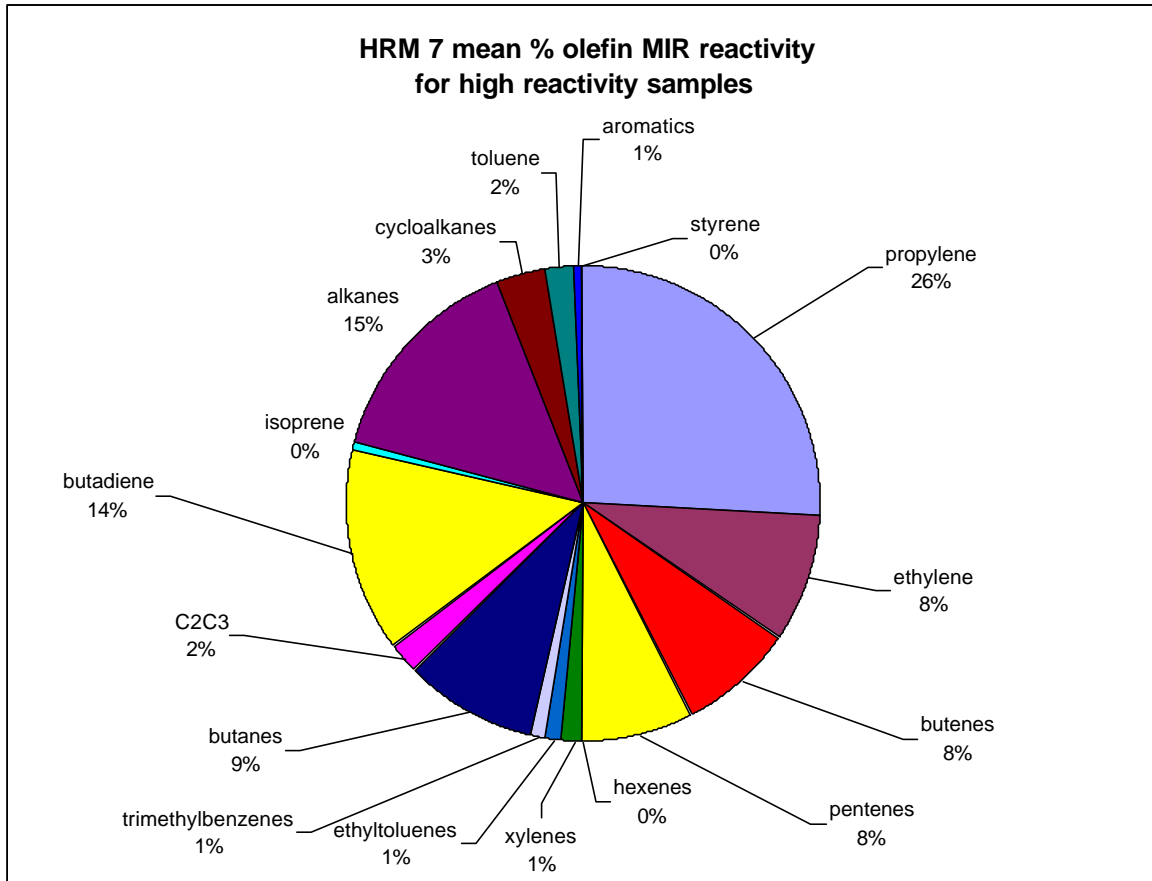


Figure 12. HRM 7 MIR reactivity for samples with total MIR reactivity > 166.

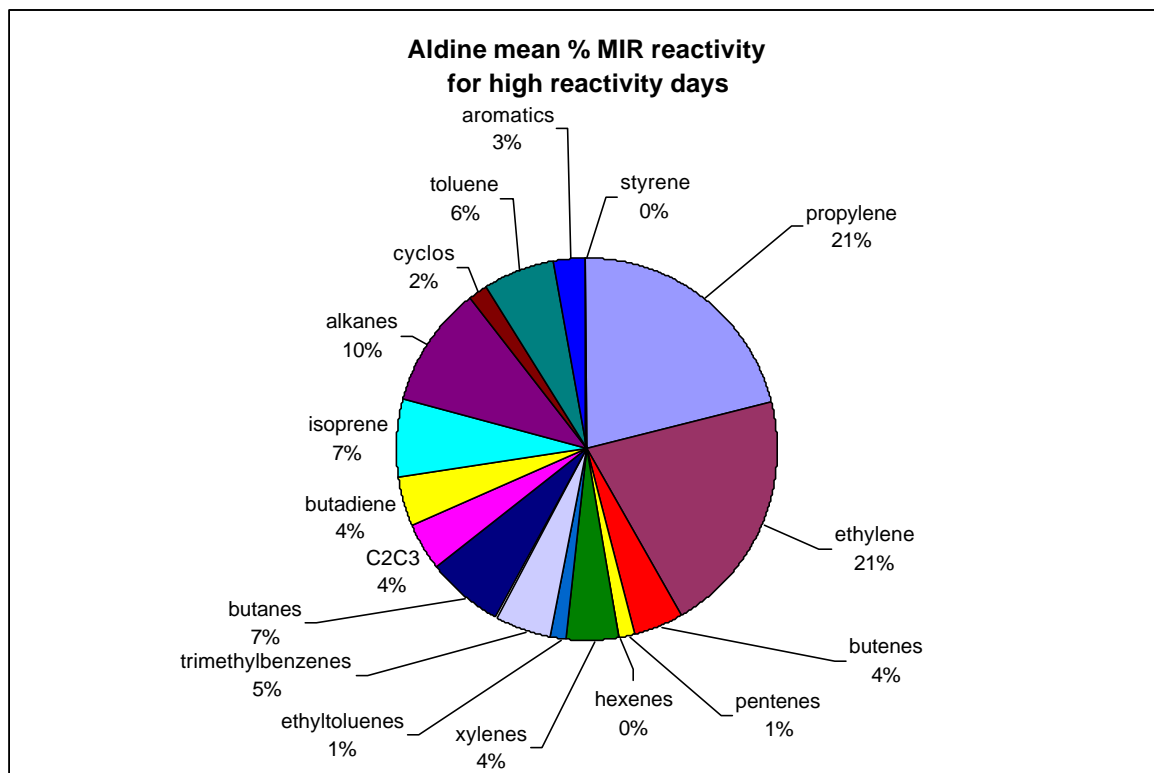


Figure 13. Aldine MIR reactivity for samples with total MIR reactivity > 166.

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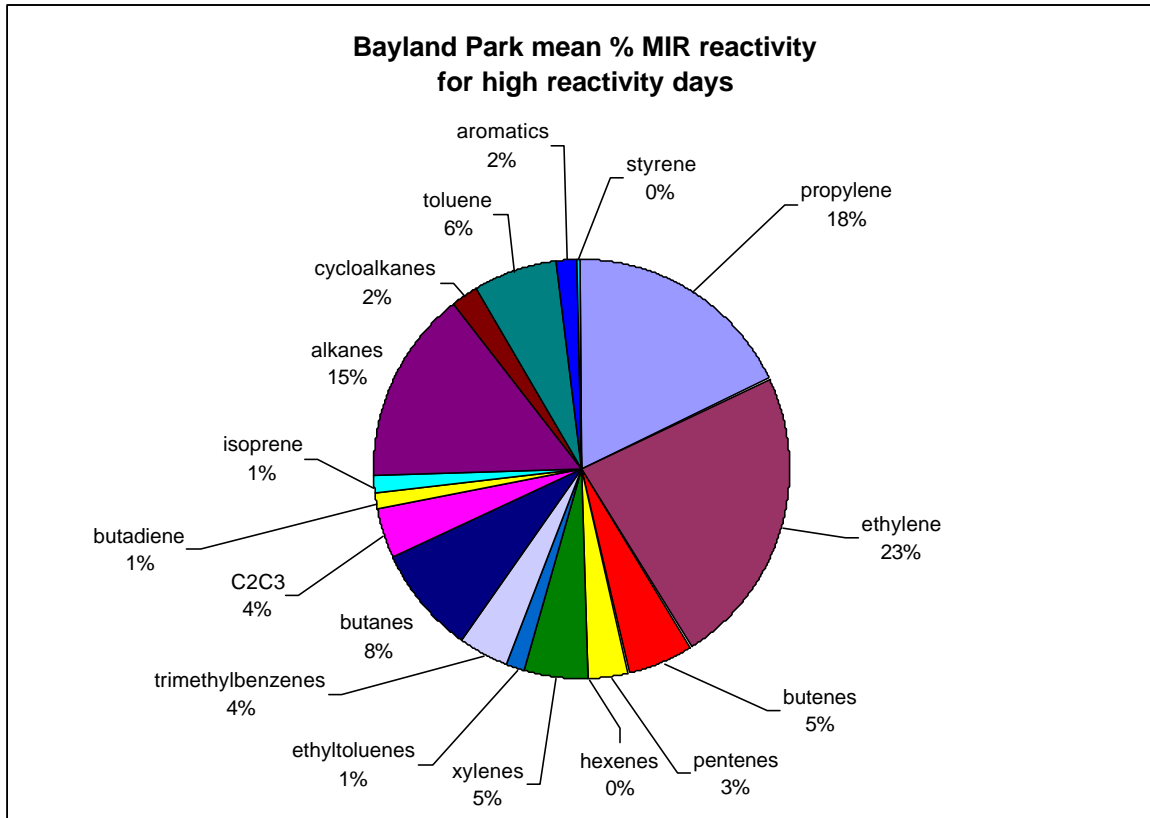


Figure 14. Bayland Park MIR reactivity for samples with total MIR reactivity > 166.

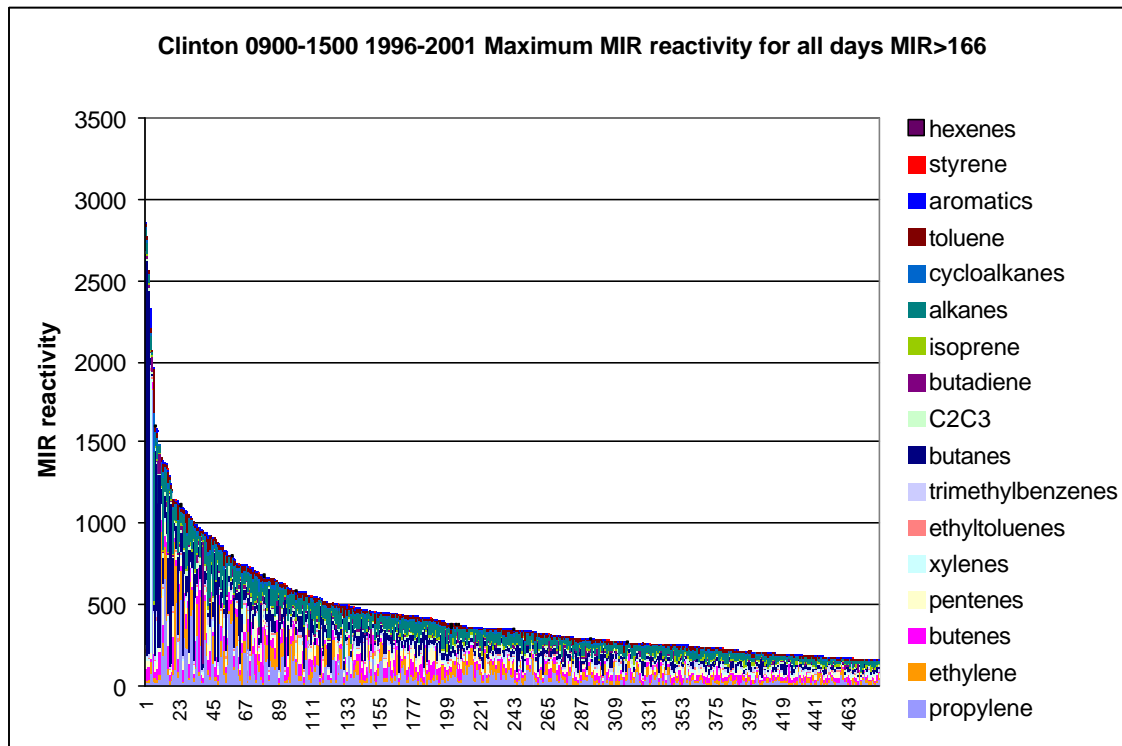


Figure 15. Clinton midday summer maximum daily MIR reactivity for high reactivity days.

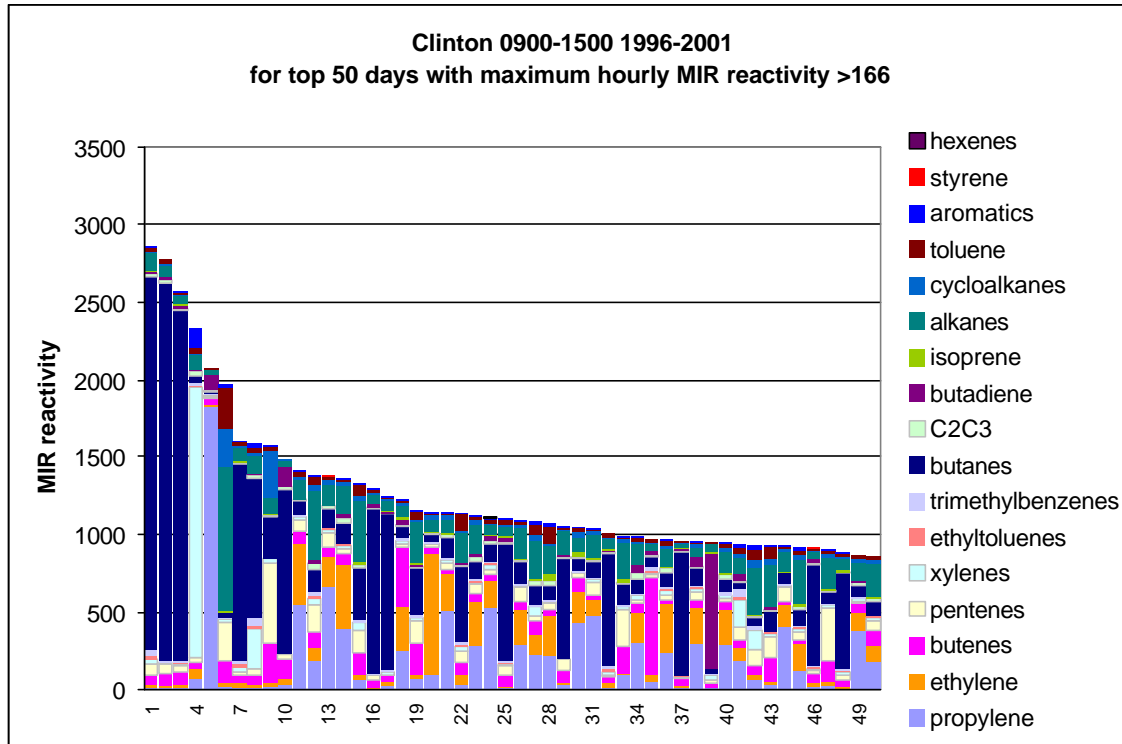


Figure 16. Clinton midday maximum daily MIR reactivity for the 50 days with highest total MIR reactivity.

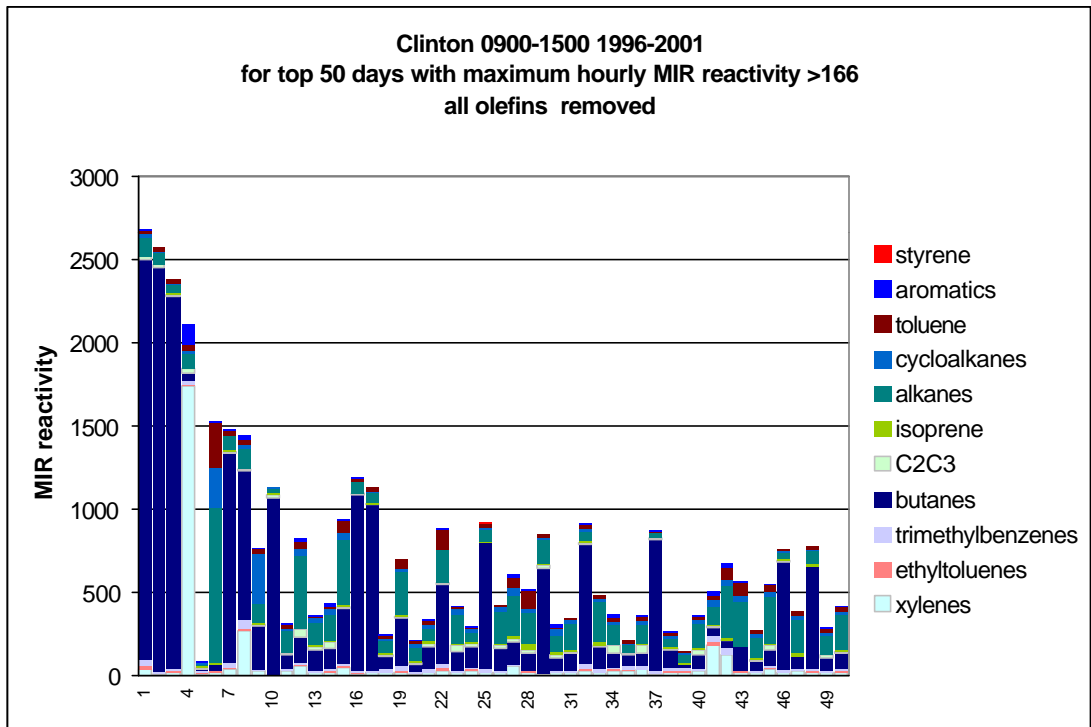


Figure 17. Same as Figure 14 above, except contribution of all light olefins has been removed.

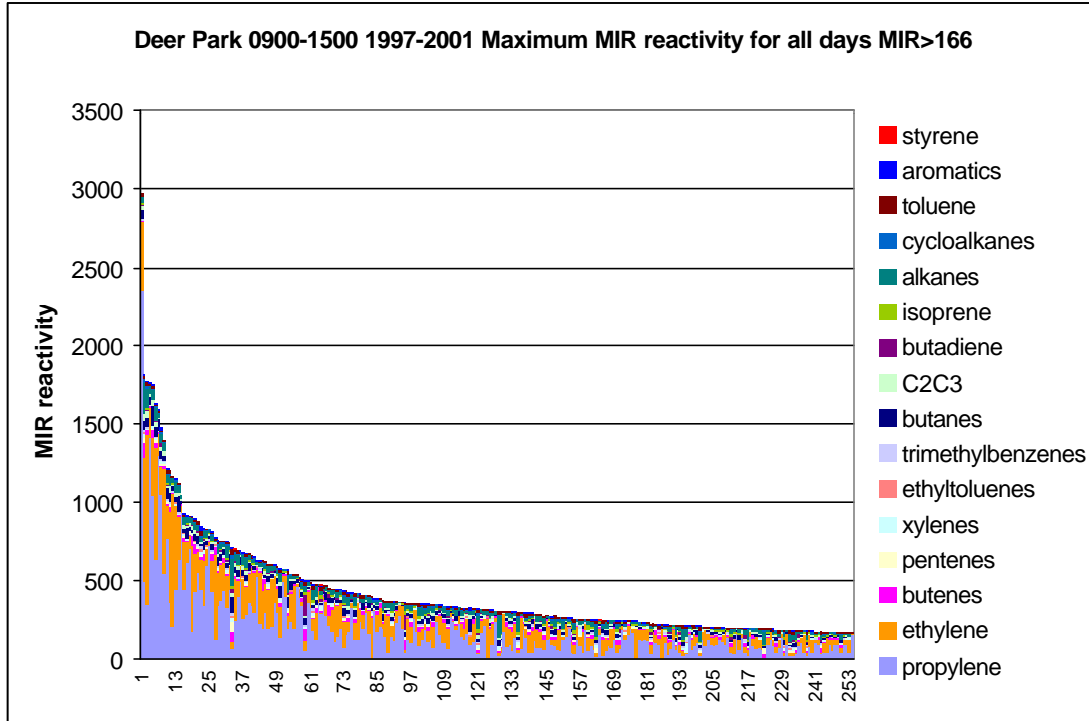


Figure 18. Deer Park midday summer MIR reactivity.

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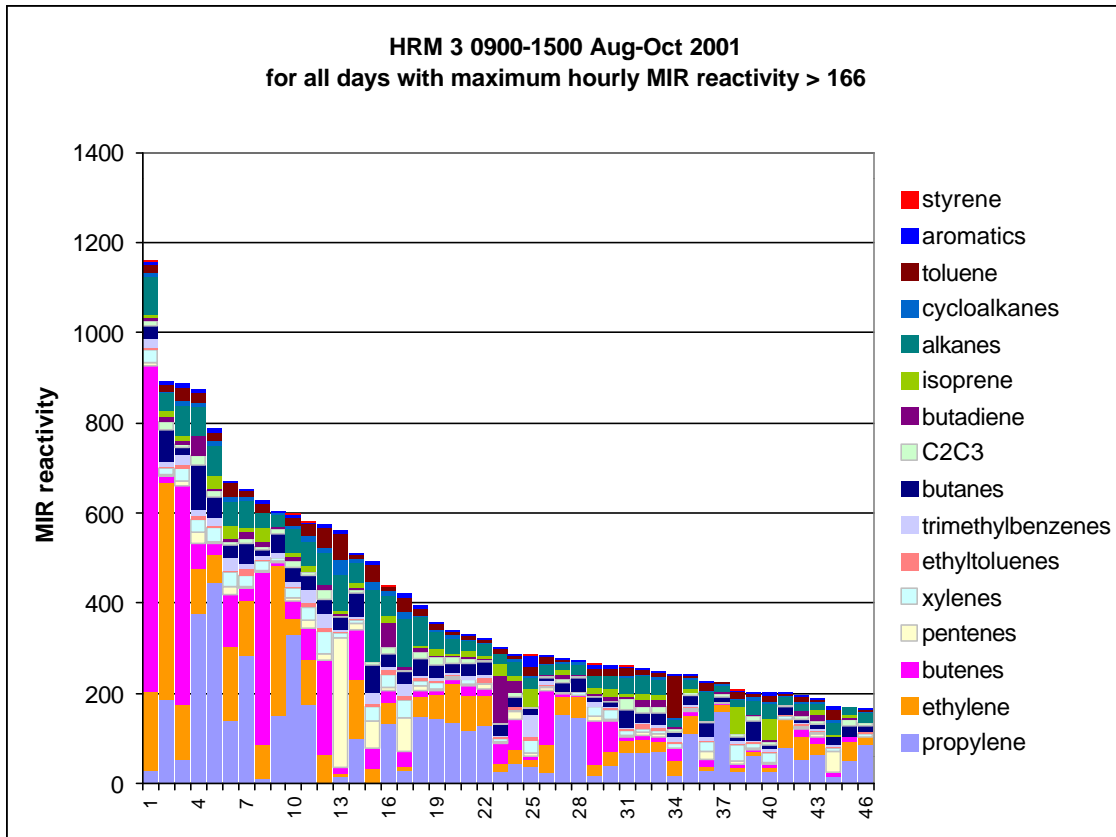


Figure 19. HRM 3 midday summer MIR reactivity.

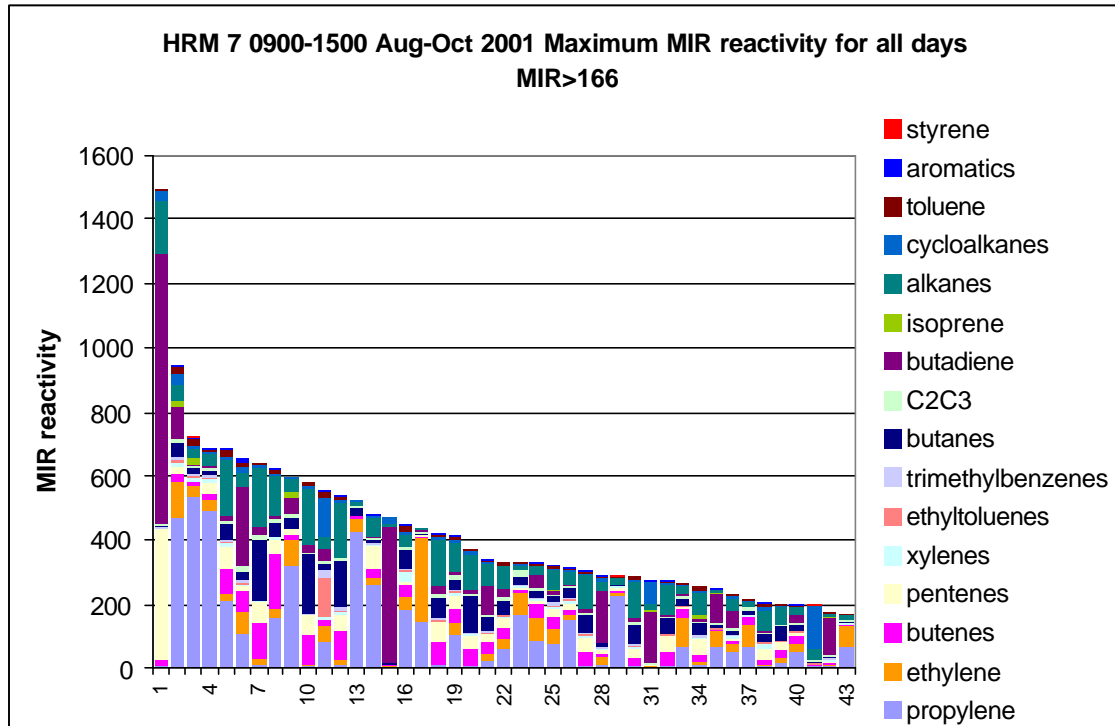


Figure 20. HRM 7 midday summer MIR reactivity.

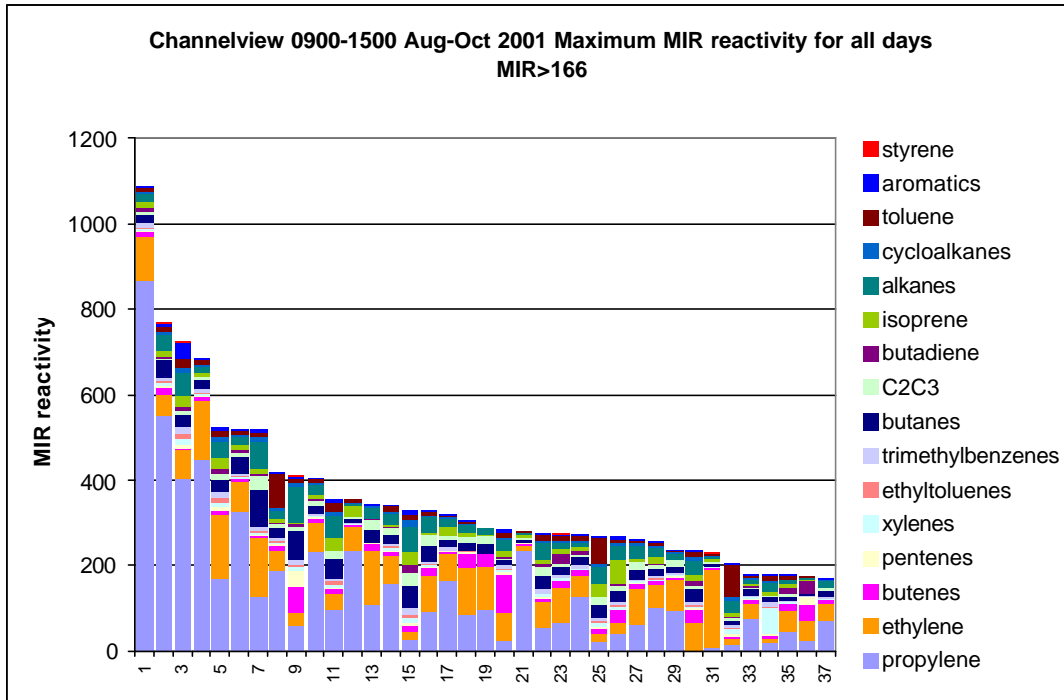


Figure 21. Channelview midday summer MIR reactivity.

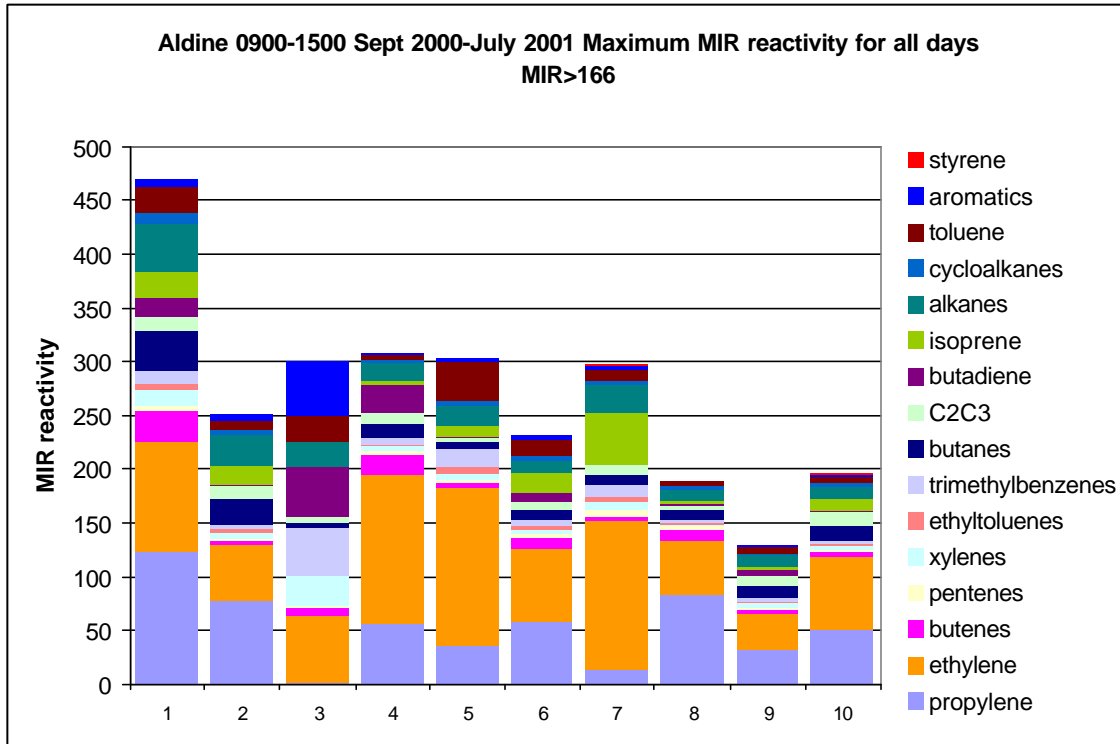


Figure 22. Aldine midday summer MIR reactivity.

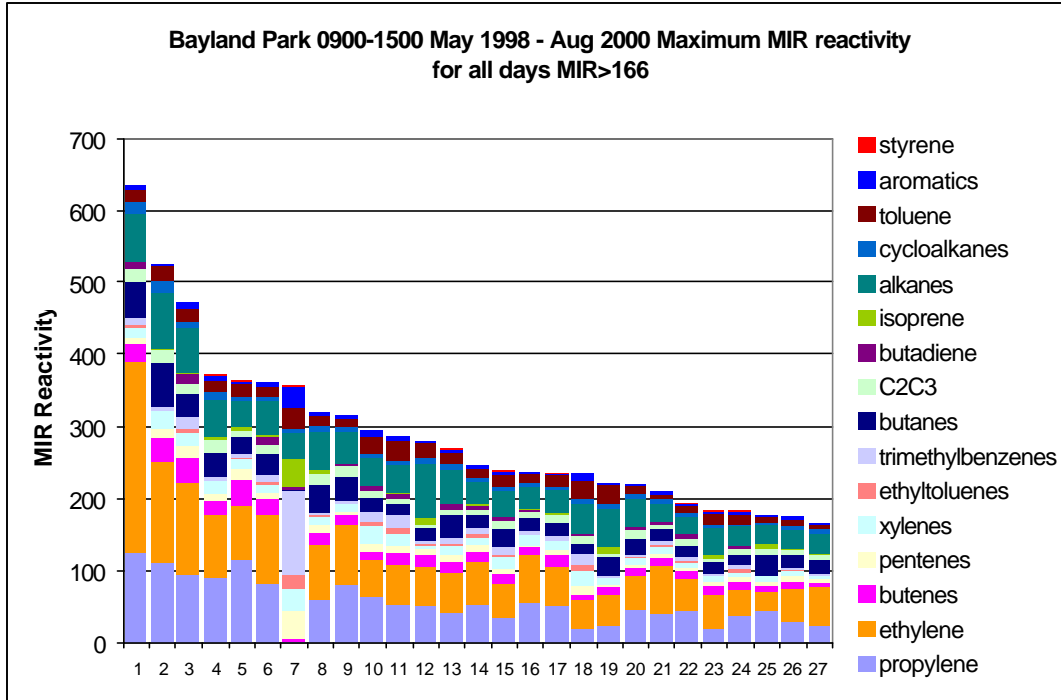


Figure 23. Bayland Park midday summer MIR reactivity.

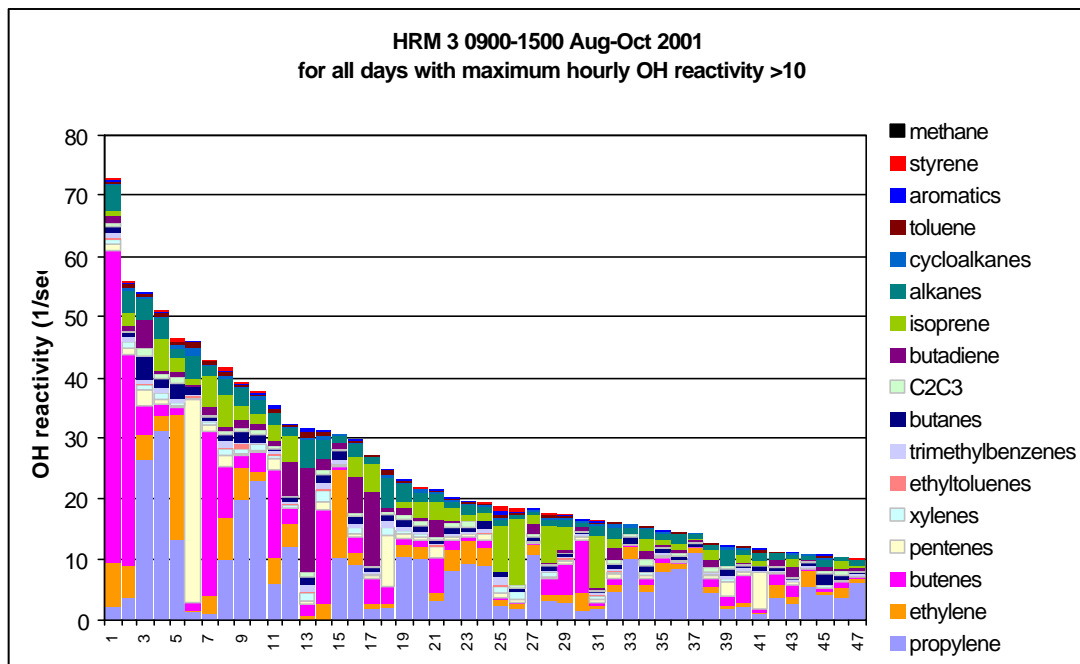


Figure 24. HRM 3 midday summer OH reactivity.

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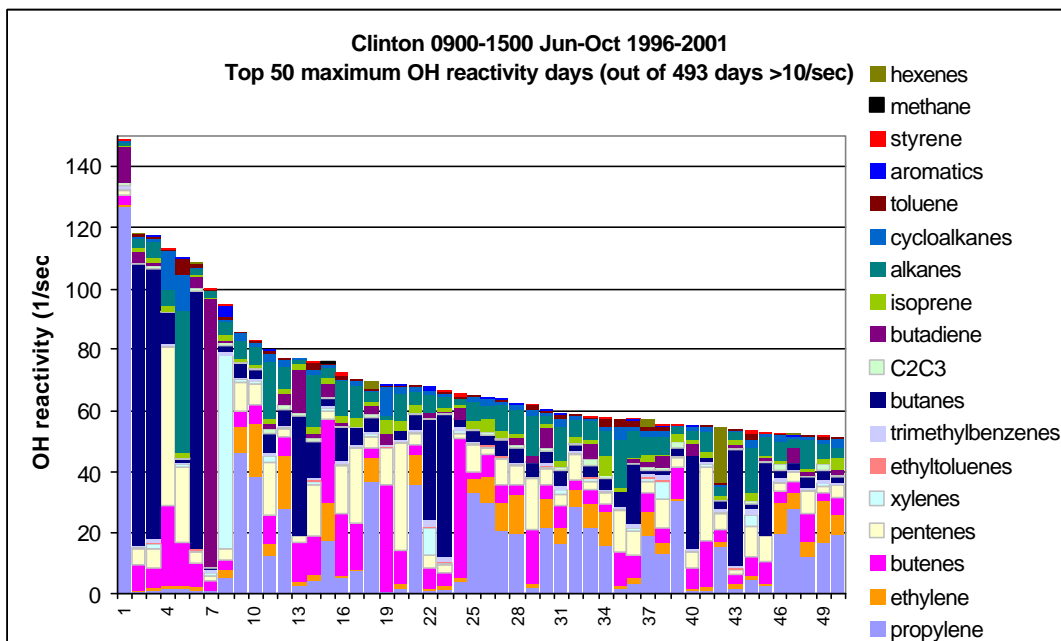


Figure 25. Clinton midday summer OH reactivity for top 50 days out of 493 total.

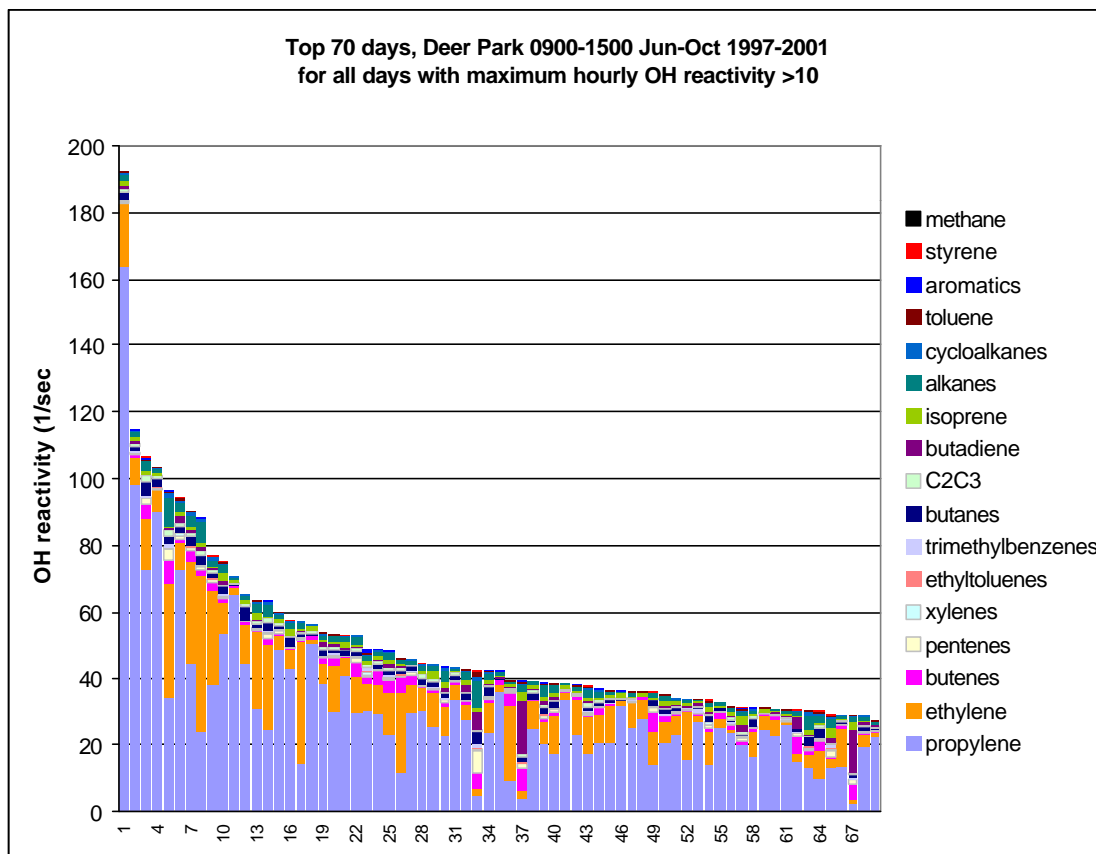


Figure 26. Deer Park midday summer OH reactivity, top 70 days out of 254 high reactivity days total.

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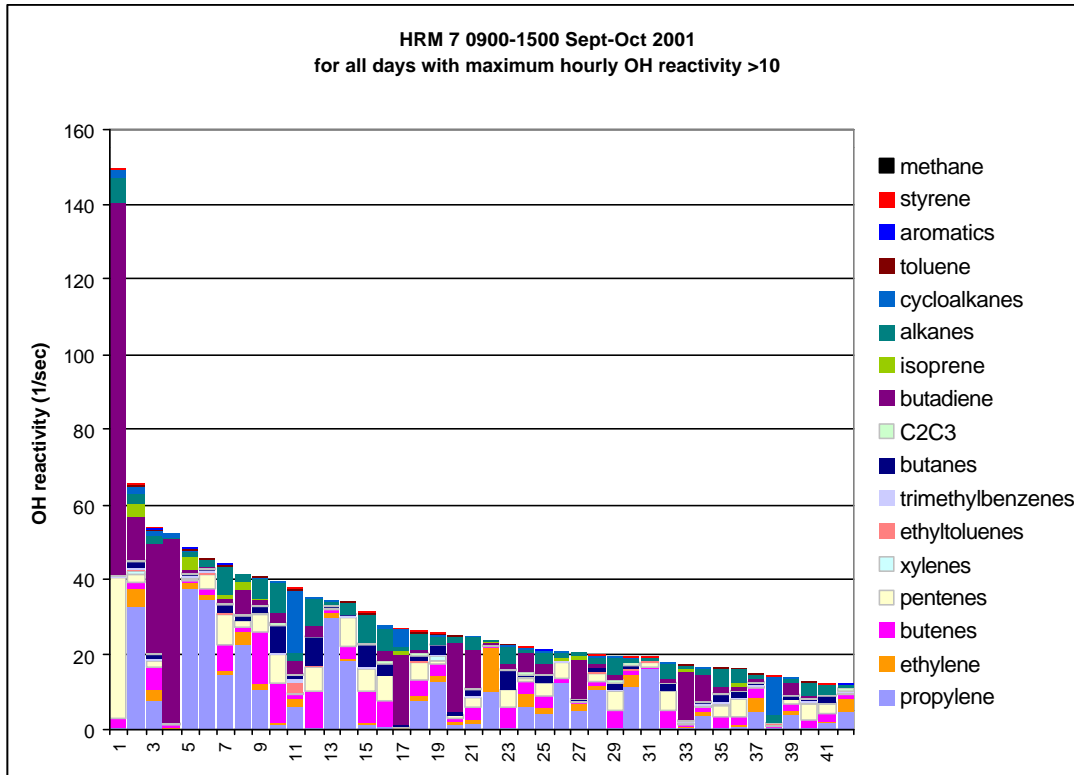


Figure 27. HRM 7 midday summer OH reactivity.

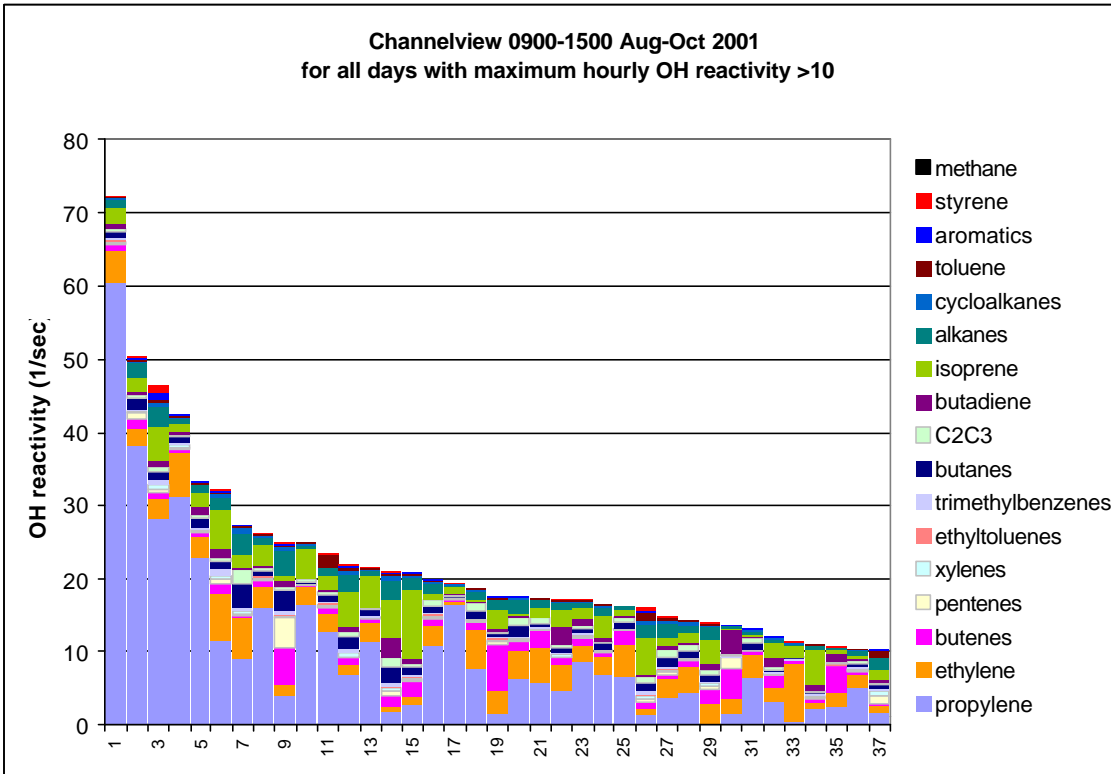


Figure 28. Channelview midday summer OH reactivity.

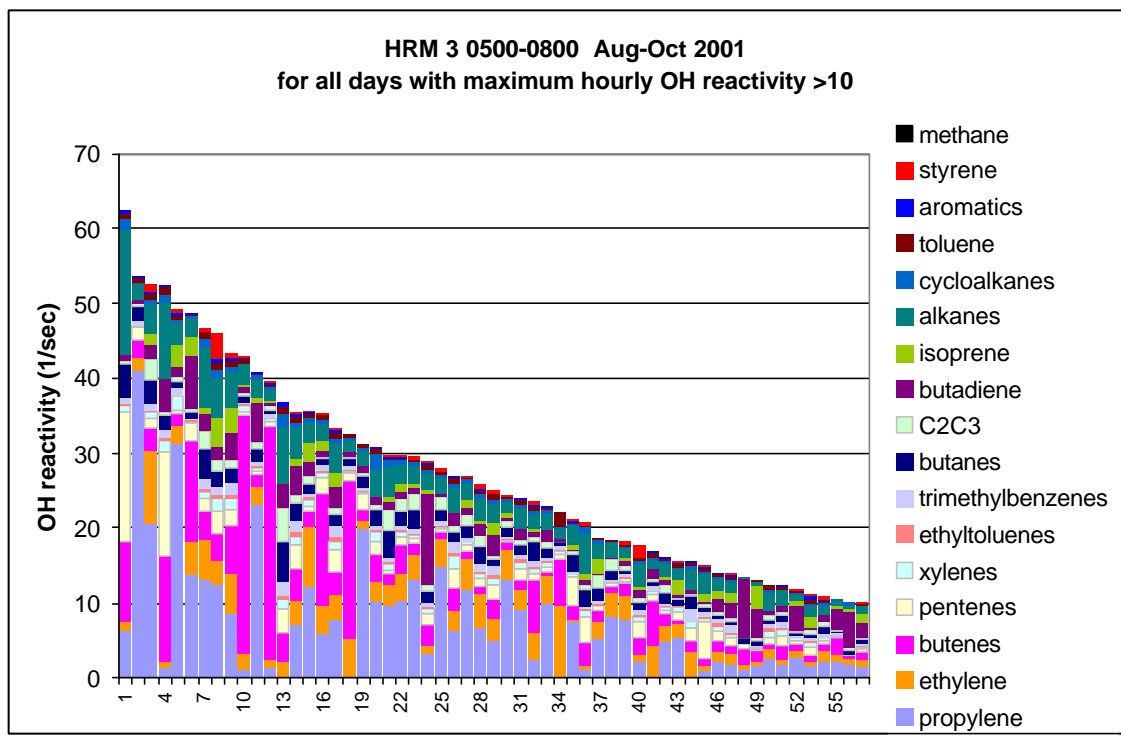


Figure 29. HRM 3 morning transition summer OH reactivity. Compare to Figure 24, HRM 3 midday summer OH reactivity.

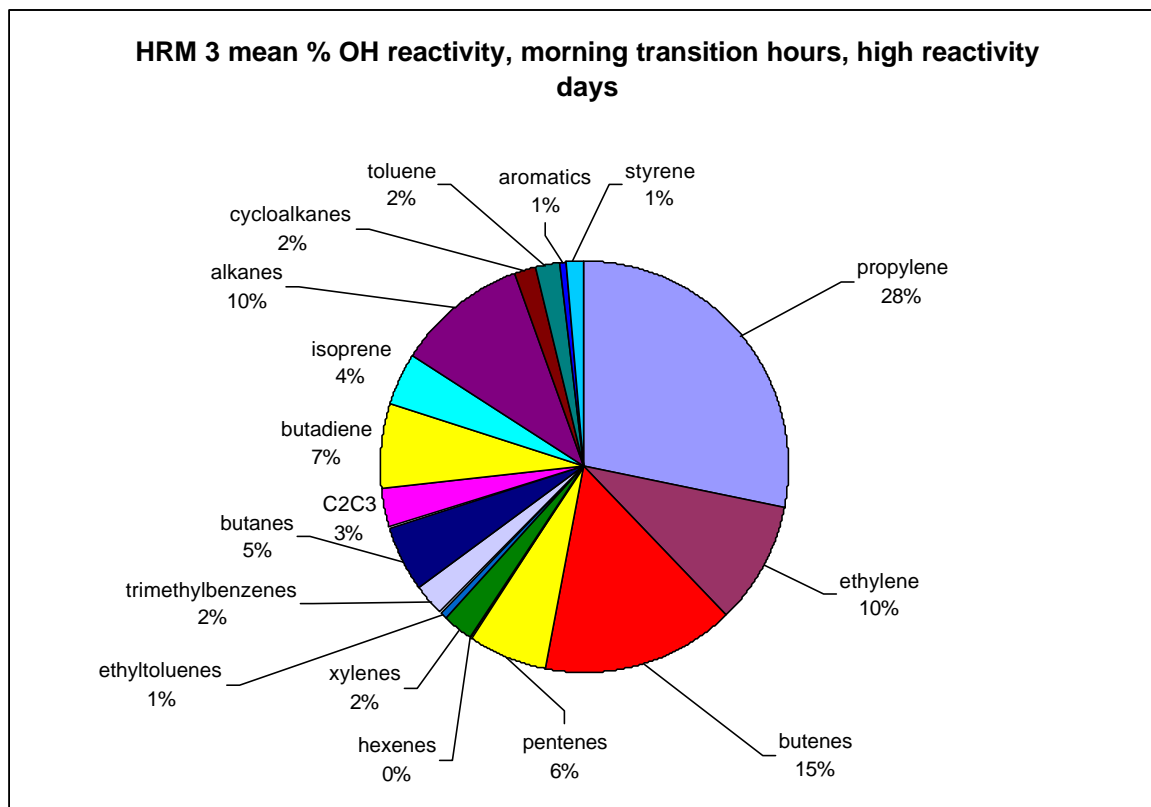


Figure 30. HRM 3 OH reactivity for morning transition hours on days with at least one hour of total OH reactivity >10. Compare to Figure 11, HRM 3 OH reactivity for midday hours on high reactivity days.

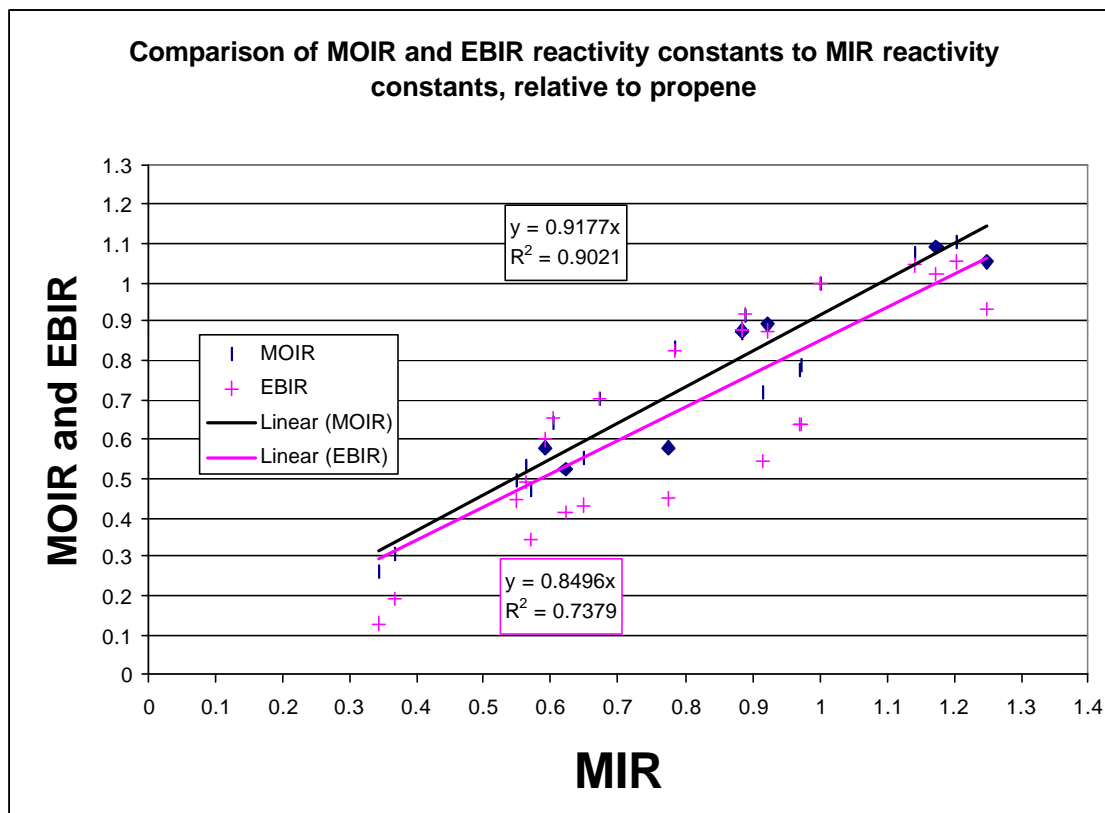


Figure 31. Comparison of additional reactivity scales to the MIR scale. The reactivity values of each VOC_i was divided by the reactivity value of propene, for three scales, MOIR, EBIR, and MIR. Then the ratios for MOIR and EBIR were plotted versus the MIR ratios. If the reactivity of every compound was constant relative to propene regardless of which scale was used, the regression lines should have a slope of 1. The MOIR slope is 0.92 and the EBIR slope is 0.85, indicating that relative to propene, most compounds have the highest reactivity value on the MIR scale. If the reactivities of these compounds were calculated with the MOIR or EBIR scales, they would be less important relative to propene.

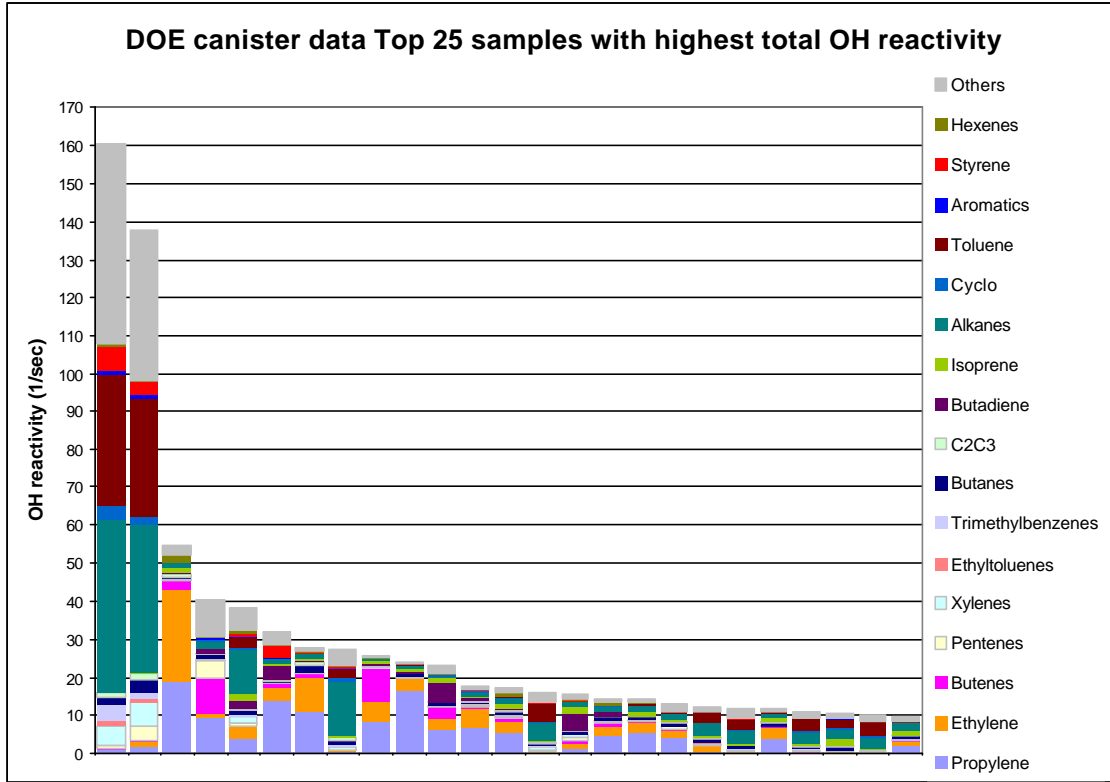


Figure 32. Brookhaven National Laboratory airborne canister OH reactivities. Note that the VOC mixture seen in the two most reactive canisters display a pattern relatively unusual compared to auto-GC observations.

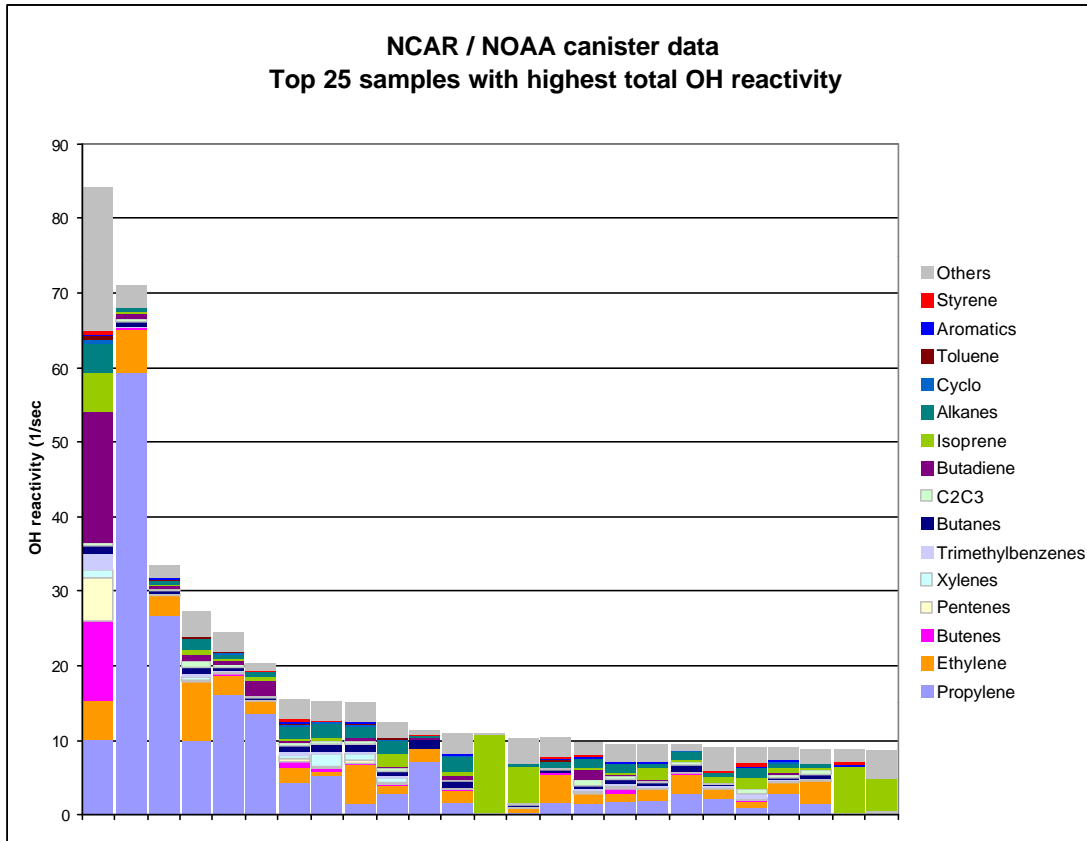


Figure 33. NCAR/NOAA airborne canister OH reactivity.

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Appendix A. OH reaction constants with PAMS VOCs.

Table 3. Atkinson's OH reactivity constants (at standard pressure and temperature).

Compound	Code	K(OH) ' 10 ⁻¹²
1- pentene	_1PNTE	31.4
1,2,3-trimethylbenzene	_123TMB	32.7
1,2,4-trimethylbenzene	_124TMB	32.5
1,3,5-trimethylbenzene	_135TMB	56.7
1,3-butadiene	_13BUIE	66.6
1-butene	_1BUTE	31.4
2,2,4-trimethylpentane	_224TMP	3.57
2,2-dimethylbutane	_22DMB	2.34
2,3,4-trimethylpentane	_234TMP	7.1
2,3-dimethylbutane	_23DMB	5.78
2,3-dimethylpentane	_23DMP	7.1
2,4-dimethylpentane	_24DMP	5
2-methyl-1-pentene	_2M1PE	63
2-methyl-2-butene	_2M2BE	86.9
2-methylheptane	_2MHEP	8.3
2-methylhexane	_2MHXA	6.9
2-methylpentane	_2MPNA	5.3
3-methyl-1-butene	_3M1BE	31.8
3-methylheptane	_3MHEP	8.6
3-methylhexane	_3MHXA	7.1
3-methylpentane	_3MPNA	5.4
acetylene	ACETY	0.815
benzene	BENZ	1.22
c-2-butene	C2BTE	56.4
c-2-pentene	C2PNE	65
cyclohexane	CYHXA	7.21
cyclopentane	CYPNA	5.02
cyclopentene	CYPNE	67
ethane	ETHAN	0.254
ethene	ETHYL	8.52
ethylbenzene	EBENZ	7
isobutane	ISBTA	2.19
isopentane	ISPNA	3.7
isoprene	ISPRE	101
isopropylbenzene	ISPBZ	6.3
m-diethylbenzene	MDEBNZ	23
methane	METHA	0.0062

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methylcyclohexane	MCYHX	10
methylcyclopentane	MCPNA	5.7
m-ethyltoluene	METOLU	18.6
m-xylene	MPXY	23.1
n-butane	NBUTA	2.44
n-decane	NDECA	11.2
n-heptane	NHEPT	7.02
n-hexane	NHEXA	5.45
n-nonane	NNON	10
n-octane	NOCT	8.71
n-pentane	NPNTA	4
n-propane	PROPA	1.12
n-propylbenzene	NPBZ	5.8
o-ethyltoluene	OETOLU	11.9
o-xylene	OXYL	13.6
p-diethylbenzene	PDEBNZ	15
p-ethyltoluene	PETOLU	11.8
propene	PRPYL	26.3
p-xylene	MPXY	14.3
styrene	STYR	58
t-2-butene	T2BTE	64
t-2-pentene	T2PNE	67
toluene	TOLU	5.63

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Appendix B. MIR values for auto-GC compounds from <ftp://ftp.cert.ucr.edu/pub/carter/SAPRC99/r99tab.xls>

Description	MIR (grams O3 / grams VOCi)
1-Pentene	7.79
1,2,3-Trimethyl Benzene	11.26
1,2,4-Trimethyl Benzene	7.18
1,3,5-Trimethyl Benzene	11.22
1,3-Butadiene	13.58
1-Butene	10.29
2,2,4-Trimethyl Pentane	1.44
2,2-Dimethyl Butane	1.33
2,3,4-Trimethyl Pentane	1.23
2,3-Dimethyl Butane	1.14
2,3-Dimethyl Pentane	1.54
2,4-Dimethyl Pentane	1.65
2-Methyl-1-Pentene	5.18
2-Methyl-2-Butene	14.45
2-Methyl Heptane	1.20
2-Methyl Hexane	1.37
2-Methyl Pentane	1.80
3-Methyl-1-Butene	6.99
3-Methyl Heptane	1.34
3-Methyl Hexane	1.85
3-Methylpentane	2.07
Acetylene	1.25
Benzene	0.82
cis-2-Butene	13.23
cis-2-Pentene	10.24
Cyclohexane	1.46
Cyclopentane	2.69
Cyclopentene	7.39
Ethane	0.31
Ethene	9.08
Ethyl Benzene	2.79
Isobutane	1.35
Iso-Pentane	1.67
Isoprene	10.69
Isopropyl Benzene (cumene)	2.32
C10 Disubstituted Benzenes	5.92
Methane	0.0139
Methylcyclohexane	1.99
Methylcyclopentane	2.42

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Description	MIR (grams O3 / grams VOCi)
C9 Disubstituted Benzenes	6.61
n-Butane	1.33
n-Decane	0.83
n-Heptane	1.28
n-Hexane	1.45
n-Nonane	0.96
n-Octane	1.11
n-Pentane	1.54
Propane	0.56
n-Propyl Benzene	2.20
C9 Disubstituted Benzenes	6.61
o-Xylene	7.49
C10 Disubstituted Benzenes	5.92
C9 Disubstituted Benzenes	6.61
Propene	11.58
p-Xylene	4.25
Styrene	1.95
trans-2-Butene	13.91
trans-2-Pentene	10.23
Toluene	3.97

pendix B (cont.) MIR values for auto-GC compounds from A p
<ftp://ftp.cert.ucr.edu/pub/carter/SAPRC99/r99tab.xls>