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Preliminary Emission Adjustment Factors Using Automated Gas Chromatography Data

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Methods

Emission adjustments were calculated for three individual compounds (ethene, propene, and 1,3-butadiene) and one group of compounds (butenes). Butenes include the three C4 alkenes measured by the auto-gcs: 1-butene, t-2-butene, c-2-butene. All compounds under study will be referred to as VOCi. Median VOCi/NO_x concentrations were calculated for 10E wind direction bins. VOCi and NO_x were in units of ppbv. Auto-gc data from five sites were used: Clinton, Deer Park, HRM3, HRM7, Channelview. All available, valid data were used in this exercise (Table 1).

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

Emissions for VOCi and NO_x were calculated in moles/day for each 10E wind direction bin, using an August 2002 extract from the TCEQ Point Source Data Base (afs_psdv_voc_2000v12a). Moles of NO_x were calculated using the molecular weight of NO₂ (42 g/mol), in accordance with TCEQ emission reporting requirements. Direction and distance from each monitoring site to each emission point were calculated using pilots' bearing equations available at <http://williams.best.vwh.net/avform.htm>. VOCi and NO_x reported emissions that fell within a given wind direction bin were summed; VOCi/NO_x emission ratios were then calculated from the sums of reported emissions within each bin.

Groups of contiguous wind direction bins were lumped together to create "wedges". The median VOCi concentrations and VOCi/NO_x ratios for each wind direction bin were used to determine emission signals from source clusters. Based upon the emission signals, wind direction bins were grouped together to represent the emissions from a given upwind area. The median VOCi and NO_x concentrations and VOCi/NO_x ratios were calculated for each wedge. Median concentrations and ratios were used to avoid over-representing extreme events.

All emission points for the compounds of interest were mapped to determine the bearing and

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distance from each monitoring site to clusters of closely-grouped emission points. Ten emission clusters were designated: Channelview, Baytown, Mont Belvieu, Bayport, East Ship Channel, East Central Ship Channel, West Central Ship Channel, West Ship Channel 1, West Ship Channel 2, and South of HRM3.

The VOC_i/NO_x ratio for emissions within each wedge was calculated by summing separately the VOC_i and NO_x for all emission points located within the wedge and within 25 km of the monitoring site. The emission adjustment factor for each VOC_i was calculated by dividing the median observed VOC_i/NO_x ratio for the wedge by the emissions VOC_i/NO_x ratio. Inferred VOC_i emissions were then calculated by multiplying the emission adjustment factor by the reported VOC_i emissions within the wedge. Wedges were named according to which cluster of emission sources they included.

Ideally, a source cluster could be characterized by itself, without interference from other clusters' emissions. A nearly ideal example is the Bayport emissions cluster, which is somewhat isolated from other clusters, and is oriented so that the Deer Park monitoring site sees a clear and unadulterated signal from the emission sources. In some cases, however, emission clusters were aligned with each other, making it difficult to develop an emission adjustment factor that applied to only one cluster. For example, the Deer Park monitoring site cannot see the emissions signal of East Ship Channel without also seeing the Baytown signal, since the two source clusters are located in the same direction at different distances. Since there were five monitoring sites, it was possible to isolate most of the emission clusters using at least one site. The major exception was the East Ship Channel cluster, which was aligned with other source clusters from the perspective of most monitoring sites. To resolve this problem, the East Ship Channel cluster's additional emissions were calculated by using a conservative emission adjustment factor from the Clinton site, which had a large amount of data characterizing the emission signal from the West Central, East Central, and East Ship Channel clusters. The East Ship Channel's contribution was then estimated by subtracting out the contributions of the West Central and East Central Ship Channel clusters, which were derived from Deer Park data.

In deciding which monitoring site's emission adjustment factors to use for each source cluster, several criteria were relied upon. The most important was the number of observations—a high number of observations (e.g., 150 hourly observations or more) gave greater confidence than a small number of observations, which are more likely to have occurred during unusual conditions. The adjustment factors for only two source clusters were developed from less than 200 hours of data: Baytown (176 hours from HRM7) and Mt. Belvieu (173 hours from HRM7). All other source clusters had adjustment factors based on at least 847 observations, up to 6833 observations. The large number of observations reduces the chance that a few unusual meteorological or emission conditions cause bias in the median values of the data.

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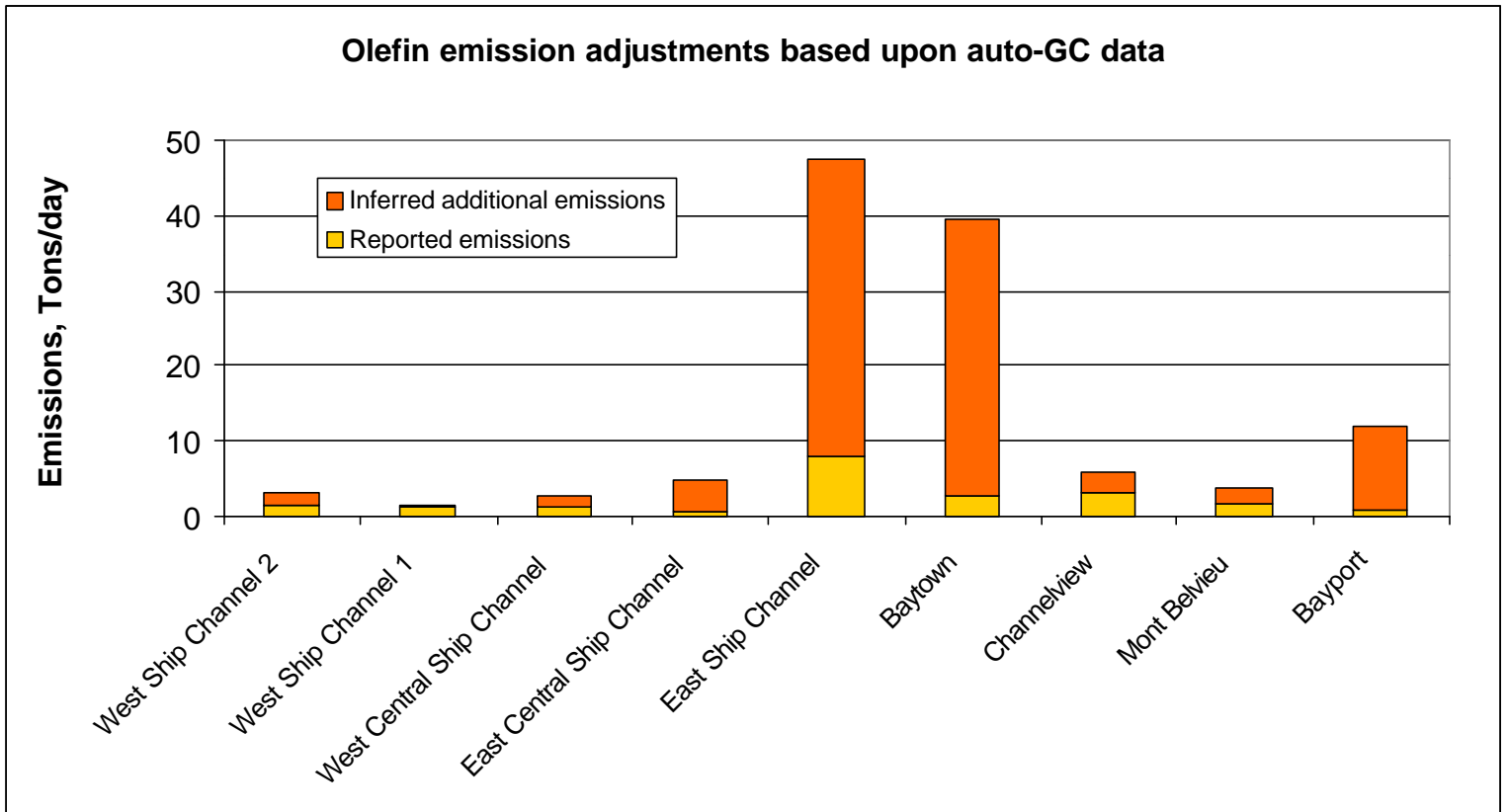
Table 2 shows preliminary emission adjustments calculated for ethylene, propylene, 1,3-butadiene, and butenes. Most adjustments fall between 2-15, except for the original Bayport adjustments, which were much larger. Further analysis of the Bayport adjustment revealed that a power plant fell barely within the wedge used to derive the original Bayport values. Since the power plant emissions were isolated from the VOC emissions, they were unlikely to mix fully with the VOCs, and therefore less likely to influence the VOC_i/NO_x ratio than the NO_x sources near the VOC sources. Therefore, the Bayport adjustment was recalculated without the power plant emissions. The revised adjustment was much lower, but still relatively large (approximately 15) compared to the other source clusters.

Application of emission adjustments to modeled emissions inventory

Inferred emissions of ethylene, propylene, 1,3-butadiene, and butenes were calculated, and summed to get a total quantity of inferred “olefin” emissions. The difference between the total inferred olefins and total reported olefins equaled the quantity that needed to be added to the modeling inventory. Table 3 and Figure 1 show the quantity of olefins added within each source cluster.

Table 3. Reported and inferred emissions for source clusters, using auto-GC data.		
Source Cluster	Reported emissions (tons/day)	Inferred emissions (tons/day)
West Ship Channel 2	1.48	3.13
West Ship Channel 1	1.22	1.51
West Central Ship Channel	1.21	2.78
East Central Ship Channel	0.66	5.00
East Ship Channel	8.10	47.5
Baytown	2.81	39.5
Channelview	3.16	5.95
Mont Belvieu	1.75	3.88
Bayport	0.92	11.9

Figure 1. Reported and inferred olefin emissions based upon analysis of auto-GC data.



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Speciation information is not completely preserved when converting to the Carbon Bond 4 lumped species. Table 4 shows the speciation of the added olefin emissions by mass percent. The speciation corresponds to the mass-weighted speciation observed in the auto-gc observations.

Table 4. Speciation of all added olefin emissions	
VOC species	Mass percentage of added olefin emissions
ethylene	46.3
propylene	34.1
1,3-butadiene	4.0
1-butene	6.1
c-2-butene	3.3
t-2-butene	5.5

Additional light olefin emissions were calculated for source clusters, not individual facilities, process units, or emissions inventory accounts. The additional emissions were assigned to accounts whose reported olefin emissions exceeded 0.1 tons/day. Additional light olefins were added to each cluster, then assigned to these selected accounts according to how much olefin emissions the accounts are currently reporting. The adjusted emissions for each account should not be construed as a prediction of how much the facility is actually emitting. Table 5 shows how the additional olefin emissions were assigned to accounts.

Discussion

For some source clusters, the reported light olefin emissions from a few large facilities comprise most of the emissions from the entire cluster. For other clusters, the reported emissions for the cluster are spread among many smaller facilities that report less than 0.1 tons/day of light olefin emissions. For the latter type of source cluster, the current method cannot determine whether the additional inferred olefin emissions are being emitted by the few largest facilities or by the many small facilities.

Three source clusters seem to be routinely emitting much more light olefins than they are reporting: East Ship Channel, Baytown, and Bayport. Baytown and Bayport emissions are dominated by only a few large facilities, whereas the East Ship Channel area has many relatively small facilities.

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Table 5. Assignment of extra olefins to accounts. *NOTE: The adjustments are not predictions about how much the named facility is actually emitting.*

Account	Name	Olefin adjustment factor	Unadjusted Olefin Emissions (tons/day)	Total Calculated Adjusted Emissions	Extra Olefins (tons/day)	Source Cluster	
HG0218K	DU PONT LAPORTE	21.02	0.13	2.97	2.83	Baytown	
HG0228H	EXXON CHEMICAL CO	21.02	0.31	6.73	6.43	Baytown	
HG0229F	EXXONMOBIL CHEMICAL CO	21.02	0.66	14.56	13.90	Baytown	
HG0232Q	EXXON MOBIL CORP	21.02	0.64	14.18	13.53	Baytown	
HG0126Q	HOECHST CELANESE CHEMICAL	13.74	0.21	3.09	2.88	Bayport	
HG0323M	MONTELL USA INC	13.74	0.25	3.70	3.45	Bayport	
HG0537O	LYONDELL CHEMICAL PASADENA	13.74	0.19	2.76	2.58	Bayport	
HG1996R	EQUISTAR CHEMICALS PASADENA	13.74	0.15	2.25	2.10	Bayport	
HG0033B	EQUISTAR CHEMICALS LP	0.89	2.93	5.52	2.59	Channelview	
HG1575W	LYONDELL CHEMICAL CO	0.89	0.23	0.43	0.20	Channelview	
HG0048L	LYONDELL CITGO REFINING L P	0.24	1.20	1.49	0.29	West Ship Channel 1	
HG0035U	MOBIL CHEMICAL CO	1.28	0.28	0.64	0.36	West Ship Channel 2	
HG0130C	VALERO REFINING TEXAS LP	1.28	0.30	0.68	0.38	West Ship Channel 2	
HG0562P	TEXAS PETROCHEMICALS LP	1.28	0.72	1.64	0.92	West Ship Channel 2	
HG0566H	PHILLIPS CHEMICAL COMPANY	1.59	0.43	1.13	0.69	West Central Ship Channel	
HX0055V	AMOCO CHEMICAL COMPANY	1.59	0.56	1.44	0.88	West Central Ship Channel	
HG0659W	SHELL OIL CO	6.99	0.62	4.95	4.33	East Central Ship Channel	
HG0036S	FINA OIL & CHEMICAL CO	10.17	0.28	3.14	2.86	East Ship Channel	
HG0175D	CROWN CENTRAL PETROLEUM	10.17	0.15	1.70	1.55	East Ship Channel	
HG0262H	KINDER MORGAN LIQUIDS	10.17	0.12	1.36	1.24	East Ship Channel	
HG0459J	LUBRIZOL CORPORATION	10.17	0.26	2.88	2.62	East Ship Channel	
HG0665E	BP SOLVAY POLYETHYLENE N AMERICA	10.17	0.89	9.90	9.02	East Ship Channel	
HG0713S	ENRON METHANOL	10.17	0.18	2.04	1.86	East Ship Channel	
HG0770G	EQUISTAR CHEMICALS LP	10.17	1.00	11.15	10.15	East Ship Channel	
HG0825G	SUNOCO LAPORTE	10.17	0.13	1.48	1.35	East Ship Channel	
HX2334A	LINDE GAS INC	10.17	0.28	3.13	2.85	East Ship Channel	
CI0006V	ENTERPRISE TEXAS OPERATING	1.82	0.11	0.32	0.21	Mont Belvieu	
CI0009P	EXXON CHEMICAL MT BELVIEU	1.82	0.13	0.37	0.24	Mont Belvieu	
CI0028L	EQUILON PIPELINE	1.82	0.18	0.51	0.33	Mont Belvieu	
HG0310V	CHEVRON CHEMICAL CO	1.82	0.75	2.11	1.36	Mont Belvieu	
HG1269J	AMOCO CHEMICALS	1.82	0.15	0.43	0.28	Mont Belvieu	
totals			14.43	108.67	94.24		
Note: Emission adjustments have been calculated for source clusters, not accounts.							
Olefins were added to each source cluster, and then assigned to accounts,							
according to how much olefin emissions the account is currently reporting.							
The "adjusted emissions" for each account should not be construed as a prediction of how much the facility is actually emitting.							

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So far, this method has been used to infer only light olefin emissions, but it can also be used to infer other VOC emissions, e.g., alkanes, aromatics, or other species measured by the auto-GCs. In future analyses, emissions will be inferred for other compounds, and these emission adjustments will be incorporated into future modeling runs.

Factors leading to potential low biases in the emission adjustments:

Reaction of VOC_i not accounted for. This preliminary analysis is restricted to highly reactive VOCs: ethylene, propylene, 1,3-butadiene, and several butenes. All of these compounds react rapidly with the hydroxyl radical and other oxidants, and therefore the mass of VOC_i will begin to decrease rapidly after emission. Because this analysis does not account for reaction, it assumes that the reported emissions will be delivered directly to the monitoring site without any degradation. The monitoring site, however, will see degraded emissions. Consequently, the emission adjustment factor is likely to be conservative—lower than if VOC reaction were accounted for. Later analyses may take into account the quantity of VOC_i lost due to reaction, which may increase the emission adjustment factors.

Dispersion not accounted for. This preliminary analysis assumes that the reported emissions are delivered directly to the monitoring site without a decrease in concentration due to dispersion. Gaussian plume theory indicates that dispersion will occur as a function of distance from the emission point to the monitoring point, and as a function of distance from the centerline of the plume. The result is that the analysis assumes all of the emitted VOC_i reaches the site. When later analyses take into account the quantity of VOC_i lost due to dispersion, the emission adjustment factors may increase.

Presence of large non-point-source NO_x sources. This analysis deals exclusively with point source emissions. If there are large sources of NO_x that haven't been included, the denominator of the emission adjustment equation will be larger than it should be. The result is that the VOC_i adjustment factor will be too low. Later analyses will include point, area, mobile and biogenic sources, so that this potential low bias can be corrected.

Factor leading to potential high biases in the emission adjustments:

Presence of large non-point-source VOC_i sources. Because this analysis includes only point sources, other types of sources that emit the VOCs in question could lead to a high bias in the emission adjustments. The most obvious type of source is mobile sources—if a wedge included a segment of a large highway such as I-10, the adjustment factor might be biased high if mobile sources emitted large quantities of ethylene, propylene, 1,3-butadiene, or butenes. Efforts have been taken to minimize the effect of mobile sources on the emission adjustments, by excluding wedge analyses that sampled areas with high traffic density. However, it was not possible to eliminate this influence completely. Later analyses will include all emission sources, so that the potential for this type of high bias can be removed.

Reaction of NO_x to NO_z. The analysis assumes that the NO_x from point sources is delivered to the monitoring site without degradation due to reaction. If the NO_x is consistently and significantly

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degraded, it could lead to high bias in the emission adjustment factor. Most monitoring sites are within 10 km of the emission points in question, however, so it is less likely that the NO_x will be converted from NO or NO_2 to one of the nitrogen reaction products such as PAN or HNO_3 .

Other factors that may influence the accuracy of emission adjustments:

Poor mixing of VOCs and NO_x from point sources. This preliminary analysis assumes that the VOCs and NO_x from point sources within a wind direction wedge are well-mixed. It is difficult to test this assumption, or to ensure that the analysis includes only well-mixed regimes. It may be possible to restrict later analyses to hours for which the stability class indicates good mixing. Plume modeling studies could also be useful in determining the potential effects of this assumption.

Wind direction is sometimes inadequate to determine where the observed VOCs and NO_x were emitted. It is known that wind direction within the Houston area shifts continually due to the Gulf Breeze circulation. The circulation can often lead to stagnation and abrupt wind shifts, so that trajectories calculated for air parcels in Houston are often curved or bent. This preliminary analysis does not directly take this effect into account, in that it relies upon wind direction rather than calculated trajectories to link observed concentrations to reported emissions. However, the analysis does indirectly account for this effect, because it is based upon median concentration signals observed in a very large data set. The median concentration is a measure of the central tendency that is not as strongly influenced by outliers or unusual events, unlike the arithmetic mean. For many of the observed signals, there is a distinct bell-shaped distribution around a central wind direction. The tails of the distribution indicate that sometimes the emissions from a given point source do not pass directly over the site, i.e., the centerline of the plume is not observed. By using the median concentrations, this method indirectly accounts for the random fluctuations of wind that might bring the emissions from other wind direction bins to the site, or brings only the edge of the emissions plume of sources located in the wind direction bin instead of the center of the plume over the monitoring site.

In addition, a check was made to determine whether each emission signal corresponded to an area of large VOC emissions. Usually, a strong emission source was found at the compass bearing where a large median concentration was found. Likewise, the comparison was done in the reverse manner as well, where strong reported emission sources were traced to the monitoring site to determine if a strong signal was found in that direction. In most cases, the observed emission signals and the locations of reported emissions matched. In one case, however, an error in the speciation profile of a refinery facility was found, due to the lack of an observed ethene signal in that direction at a nearby monitoring site.

Therefore, the problem of using wind direction alone to link emissions to observed concentrations has been indirectly accounted for by using the median concentrations of very large data set.

Conclusions

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Emission signals detected in automated gas chromatography data suggest that reported emissions of light olefins are routinely underestimated, sometimes by as much as a factor of 15. The source clusters that seem to be underestimating emissions by the largest factor are found in the eastern end of the Houston Ship Channel, in the Baytown area, and in the Bayport area. The uncertainties in this preliminary analysis can be reduced by focusing on observations taken during well-mixed meteorological conditions, and accounting for dispersion and non-point VOC and NO_x sources.

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Table X. "Best" estimate of emission adjustment factors for highly reactive light olefins. The "best" estimates are based upon the data described in columns 2 and 3; the range is based upon adjustments calculated from all appropriate sites.										
Source cluster	Number of observations	Monitoring site used	Ethene factor	Ethene factor range	Propene factor	Propene factor range	Butenes factor	Butenes factor range	Butadiene factor	Butadiene factor range
West Ship Channel 1	1518	Clinton	0.95	0.95 - 2.5	1.6	1.6 - 4.1	2.5	1.6 - 4.7	0.67	0.67 - 2.1
West Ship Channel 2	6833	Clinton	2.4	1.7 - 2.5	2.0	2.0 - 4.1	2.8	1.6 - 4.7	0.55	0.55 - 2.1
East and central Ship Channel	1214	Clinton	7.6	2.4 - 14	5.0	4.5 - 21	5.4	3.8 - 5.5	3.6	1.4 - 7.9
Channelview	1572	Clinton	4.2	1.8 - 20	1.9	1.1 - 9.7	0.94	0.47 - 4.0	0.49	0.28 - 17
Bayport	3421	Deer Park	32	NA	36	NA	40	NA	14	NA
Bayport revised			12	NA	14	NA	15	NA	5.4	NA
South of HRM3	847	Clinton	9.4	9.4 - 10.3	4.5	3.4 - 4.5	0.46	0.46 - 15	0.18	0.18 - 3.7
Baytown	176	HRM 7	9.6	NA	16	NA	19	NA	8.5	NA
Mont Belvieu	173	HRM 7	1.2	1.2 - 5.8	2.8	2.3 - 3.2	3.1	3.1 - 4.5	96	4.3 - 96