ENVIRON

MEMORANDUM

To: Cindy Murphy and Dave Allen, UT

From: Till Stoeckenius and Greg Yarwood

Date: 10/7/2004

Subject: Potential co-benefits of HRVOC controls at mid-sized propylene units in Houston

---

Introduction

Emissions of highly reactive volatile organic compounds (HRVOCs) have been shown to play a key role in the formation of peak ozone concentrations in the Houston-Galveston area. In the latest round of revisions to the State Implementation Plan for ozone, the Texas Commission on Environmental Quality (TCEQ) has proposed placing additional restrictions on HRVOC emissions designed to help reduce ozone levels. While the proposed regulations are designed to restrict emissions of a specific set of hydrocarbon species (namely HRVOCs), it has been postulated that the methods which will likely be employed by industry to limit the release of these species will have the added benefit of lowering emissions of other, generally less reactive, hydrocarbon compounds that are co-emitted with the HRVOCs and that can, despite their generally lower reactivities, contribute to ozone formation. Little is currently known about the magnitude of this potential co-benefit of HRVOC reductions, making it difficult to determine the ozone reductions likely to be achieved through future HRVOC controls. In this memo we examine the potential co-benefit of HRVOC emission reductions via analysis of a speciated VOC emissions database for propylene production plants in Houston area compiled by TCEQ.

Data on Emissions Speciation at Propylene Units

A search of the point source emissions database by TCEQ's Industrial Emissions Assessment Section conducted in May, 2003 identified a set of emission records for mid-sized propylene production facilities associated with seven air permit accounts in the Houston area (**Table 1**). Generally speaking, TCEQ selected emission paths by searching for all Facility Identification Numbers (FINs) at these accounts with a plant identification number including "PP" or with facility names that included "POLYP" or "PP". Additional facilities (such as emergency generators, pellet dryers, and powder loaders) with an SCC associated with polypropylene were added to the search results.

Data gathered by TCEQ include daily average emissions of propylene and other VOCs for the summer ozone season (see **Table 2**). Speciation of VOCs varies from source to source depending on what is known about the emitting process and the degree of care taken in reporting speciated emissions. Of the seven accounts examined, two (Dow Brazoria and Amoco Cedar Bayou) had a relatively high percentage of their total VOC emissions reported as "unspeciated", that is, either as contaminant code 50001 (Non-methane VOC – U) or 59000 (VOC Gas Mixture – U). In addition, reported propylene emissions at Dow Brazoria represent an insignificant fraction of total VOC from this account. These two plants differ significantly in these respects

Golden Gate Plaza • 101 Rowland Way • Novato, California 94945-5010 USA
Tel: (415) 899-0700 • Fax: (415) 899-0707

from the remaining five plants. Therefore, to avoid biasing results, Dow Brazoria and Amoco Cedar Bayou were excluded from further analysis.

Total mass emissions from all FINs meeting TCEQ's selection criteria are summarized in **Figure 1**. Propylene accounts for just over half of total VOCs from these facilities. Of the remaining VOC, over half is hexane. Only two other individual VOC species accounted for more than 2.5% of the total: propane (5%) and ethane (3%). Remaining identified VOC species total 10% whereas unspeciated VOCs account for just 3%. As shown in **Table 3**, there are ten different species which each account for more than 0.5% of the total VOC. This includes the four species shown in Figure 1 (propylene, hexane, propane and ethane) and six other species, including one other HRVOC (ethylene) which represents 2% of the total.

What if HRVOCs are Controlled at the Plant Level?
The emission speciation shown in **Figure 1** and listed in **Table 3** represent totals over all FINs identified by TCEQ as being associated with propylene production. Not all of these FINs, however, are associated with propylene emissions. For example, the database includes emissions from pellet driers and sewer vents that are associated with the polypropylene production unit but which themselves have no identified propylene emissions. Nevertheless, if plant operators achieve HRVOC emission targets by making across-the-board adjustments via plant-wide control measures, then these results indicate that, for example, a 100 lb reduction in propylene will be accompanied by a 92 lb reduction in other VOCs, including a 53 lb reduction in hexane and a 4 lb reduction in ethylene.

What if HRVOCs are Controlled at the FIN or EPN Level?
The potential co-benefits of propylene control measures described above may differ from the actual co-benefits if such controls are more specifically targeted towards just those FINs or EPNs which actually emit propylene. To examine this possibility, we computed total emissions over just those FINs with non-zero propylene emissions. The resulting distribution of emissions across species is shown in **Figure 2**; **Table 4** lists the contributions of all VOC species contributing at least 1% to the total VOC emissions. These results are roughly similar to those described in the previous paragraph with propylene accounting for a bit more than half of the total VOC and hexane accounting for just over half of the remainder. Non-speciated VOC emissions account for just 1.3%. We also examined the scenario under which propylene emissions are assumed to be controlled at the point of release by re-computing these results for all EPNs (rather than FINs) with non-zero propylene emissions (see **Figure 3** and **Table 5**). Comparison of these results with the sums over FINs with non-zero propylene shows that the choice of FIN vs EPN as the control point has little impact on the relative contribution of each VOC species.

Findings and Conclusions
Results presented above indicate that fairly significant co-benefits in the form of reduced emissions of less reactive VOCs are likely to be achieved by measures taken to reduce propylene emissions at polypropylene production plants in the Houston area. Emissions of total VOCs other than propylene would be reduced by a factor ranging between 1:1.1 to 1:1.4 relative to propylene (i.e., 1 lb reduction of other VOC for every 1.1 to 1.4 lb reduction in propylene). Due

to the process by which propylene is produced, the largest proportionate reductions (ranging between 1:1.8 to 1:2.4) would be for hexane. These results are not greatly influenced by unspeciated VOC emissions in the database. However, the emission estimates on which they are based are circa 2001 and it is likely that more complete and accurate speciated emissions data are currently available in TCEQ's point source database (PSDB). It would therefore be useful to repeat these calculations based on an updated search of emission records associated with propylene (or polypropylene) production in the current PSDB.

Table 1. Results from TCEQ's search of mid-sized polypropylene unit emissions.

Plant	Account Name	TCEQ air account number
BP Chocolate Bayou	BP Amoco Chocolate Bayou	BL0002S
Dow Brazoria	Dow Chemical, Plant B (Brazoria)	BL0082R
Exxon Baytown	2000 Exxon Baytown Chemical	HG0229F
Phillips Houston	Phillips Chemical, ouston	HG0566H
BP Solvay	BP Solvay	HG0665E
Amoco Cedar Bayou	Amoco Cedar Bayou	HG1269J
Atofina	Atofina Petrochemicals, La Porte	HG0036S

Table 2. Speciation of VOC emissions (ozone season lb/day) for each account (shaded rows indicate accounts with large amounts of non-speciated VOCs).

Plant	Total VOC	Propolyene (lb/day)	Propolyene (%)	Non-Speciated VOC (lb/day)	Non-Speciated VOC (%)
BP Chocolate Bayou	1,929.1	712.9	37.0%	81.4	4.2%
Dow Brazoria	2,078.5	1.5	0.1%	469.7	22.6%
Exxon Baytown	684.1	383.0	56.0%	16.7	2.4%
Phillips Houston	427.6	366.1	85.6%	0.5	0.1%
BP Solvay	1,658.1	1,168.5	70.5%	19.7	1.2%
Amoco Cedar Bayou	695.8	149.5	21.5%	528.4	75.9%
Atofina	633.8	147.3	23.2%	30.5	4.8%

Table 3. Emissions of VOC species individually accounting for more than 0.5% of total VOC emissions over all sources (ozone season average day).

Species	Lb/day	%
Propylene	2,778	52.1%
Hexane	1,537	28.8%
Propane	262	4.9%
Ethane	158	3.0%
Alboline1	119	2.2%
Ethylene	109	2.0%
Isobutanol	72	1.4%
Tert Butyl Alcohol	58	1.1%
Isobutane	54	1.0%

1 Alboline is a mineral oil that is not classified as a VOC.

Table 4. Emissions of VOC species individually accounting for more than 1% of total VOC emissions over all processes (FINs) with non-zero propylene emissions (ozone season average day).

Species	lb/day	% of Total VOC
Propylene	2778	58.1%
Hexane	1211	25.3%
Propane	262	5.5%
Ethane	158	3.3%
Ethylene	104	2.2%
Isobutanol	68	1.4%
Tert Butyl Alcohol	58	1.2%
Isobutane	54	1.1%

Table 5. Emissions of VOC species individually accounting for more than 1% of total VOC emissions over all emission points (EPNs) with non-zero propylene emissions (ozone season average day).

Species	Lb/day	% of Total VOC
Propylene	2907	57.9%
Hexane	1221	24.3%
Propane	278	5.5%
Ethane	158	3.1%
Ethylene	109	2.2%
Isobutanol	68	1.3%
Tert Butyl Alcohol	58	1.1%
Isobutane	54	1.1%

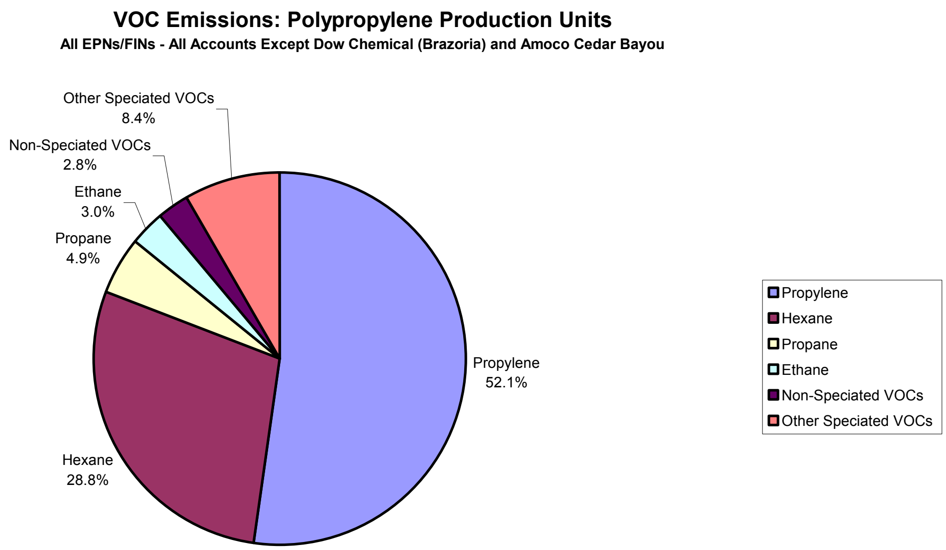

Figure 1. Speciation of VOC emissions (ozone season average day) from all emission paths associated with polypropylene production at five large petrochemical complexes in the Houston area.

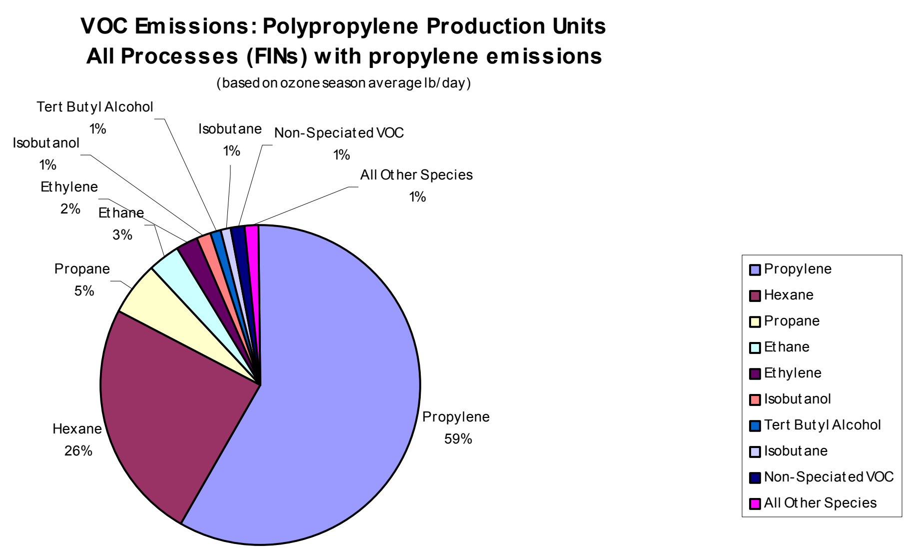

Figure 2. Speciation of VOC emissions from all processes (FINs) with non-zero propylene emissions.

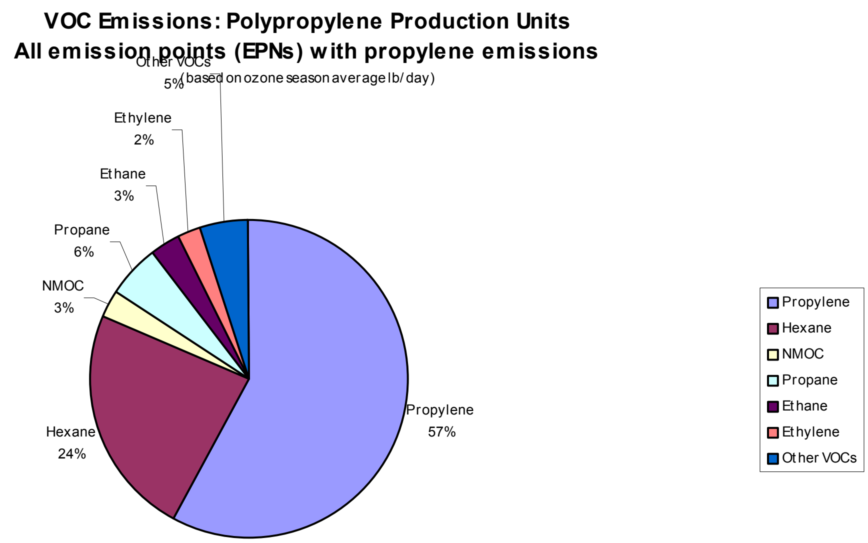

Figure 3. Speciation of VOC emissions from all emission points (EPNs) with non-zero propylene emissions.