




UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, NC 27711


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OFFICE OF
AIR QUALITY PLANNING
AND STANDARDS

MEMORANDUM

SUBJECT: Revisions to the Photochemical Assessment Monitoring Stations Compound Target List

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TO: State and Local Monitoring Agencies

The purpose of this memorandum is to summarize changes being made to the Photochemical Assessment Monitoring Stations (PAMS) compound target list. Prior to this change, the PAMS target list contained 57 compounds. This memorandum divides the previous list into two categories – priority compounds and optional compounds. In addition, seven new compounds are being added to the target list as priority compounds. Table 1 contains the revised target list. The list contains 34 priority compounds and 29 optional compounds.

The revisions to the target list are a product of a collaborative effort by EPA and state and local monitoring agencies. A workgroup was formed to evaluate the target list comprised of EPA representatives (EPA-OAQPS, EPA-ORD, and EPA-Regions 1, 2, 3, 6, 8, 9) and state and local monitoring agencies (including Arizona, City of Denver, Georgia, LADCO, Maine, Maryland, Massachusetts, New York, Texas, and South Coast AQMD). In addition, the EPA consulted with the Clean Air Science Advisory Committee's Air Monitoring and Methods Subcommittee (CASAC-AMMS) on potential revisions to the target list. Finally, the revised list has been reviewed by the National Association of Clean Air Agencies' Monitoring Steering Committee (MSC).

EVALUATION OF EXISTING TARGET COMPOUNDS

The existing target compounds were evaluated to determine if any of the existing compounds could be removed, or made optional, due to low importance. A decision matrix was used to rank the relative importance of each compound based on several criteria. A decision matrix allows for assigning importance to a compound by scoring each compound based on one or more factors. The initial score is multiplied by a weighting for the factor being evaluated. The weighted score for each factor is then summed to provide a total score for each compound. Figure 1 summarizes the results of the decision matrix analysis for the PAMS target compounds where the compounds are sorted from highest importance to least importance. The factors considered in this analysis, and relative weight assigned, included:

- Overall reactivity adjusted average concentration (30 percent);
- Reactivity adjusted average concentration during 9 am morning rush hour on high ozone days (30 percent);
- Reactivity adjusted average concentration based on geography (e.g., NE, SE, SW, MW, W) (30 percent);
- If the compound was a hazardous air pollutant (HAP) (5 percent); and
- If the compound was a high priority secondary organic aerosol precursor (5 percent).

The first three factors attempt to identify the compounds most important to ozone formation. The last two factors recognize that the measurements of the target compound may be important for other air quality programs. The rationale for selecting each factor and the approach used to score the target compounds for each of the factors are summarized in the following paragraphs.

Overall Reactivity Adjusted Average Concentration

The overall reactivity adjusted average concentration was selected as a factor to represent the importance of the compound to ozone formation. In general, higher Volatile Organic Compound (VOC) concentrations lead to increased ozone formation potential. The 2010 PAMS data (downloaded from the AQS system) was used to calculate average concentration for each target compound. For each compound the data from all sites and days were averaged. Due to differences in reactivity of the individual target compounds, the measured concentrations for each compound were multiplied by the Maximum Incremental Reactivity (MIR, Carter 2010) of the compounds to obtain their overall average reactivity adjusted concentration.

Each compound was then scored based on a proportional weighting, where the compound with the highest reactivity adjusted average concentration was awarded 100 points, and the compound with the average score was awarded 0 points. Those compounds in between the highest and lowest were scored based on the following calculation:

$$\text{Score} = (\text{Target Average} - \text{Minimum}) / (\text{Maximum} - \text{Minimum}) * 100$$

Where:

Target Average = the average MIR adjusted concentration for the compound being scored

Minimum = the lowest average MIR adjusted concentration for all compounds

Maximum = the highest average MIR adjusted concentration for all compounds

Figure 2 summarizes the scores for each target compounds based on the overall average MIR adjusted concentration.

Reactivity Adjusted Average Concentration During 9 am on High Ozone Days

This factor was selected in recognition that for some VOC compounds, their concentration (and therefore their importance to ozone formation) may be higher during high ozone episodes than at other times of the year. Only data from days where the maximum 8-hour ozone concentration exceeded 75 ppb in the county the PAMS site was located in were used in an attempt to better identify those

compounds which are most responsible for elevated ozone concentrations. In addition, only the data collected during the 9 am hour (near the end of the “morning rush hour”) was used to further focus on those compounds that would be most responsible for ozone formation during that high ozone day as it represents concentrations during the morning rush hour and concentrations present as ozone formation is beginning to increase. The data for each compound were then averaged across all sites, and then multiplied by their respective MIR value to give the reactivity adjusted average concentration during 9 am on high ozone days. Each compound was then scored based on a proportional weighting as described above. Figure 3 summarizes the reactivity adjusted average concentrations for the target compounds during the 9 am hour on high ozone days.

Reactivity Adjusted Average Concentration Based on Geographic Location

This factor was selected in order to recognize that some target compounds may be more important to ozone formation in certain parts of the country than in others. The 2010 PAMS data were divided into five geographic regions (i.e., NE, SE, MW, SW, and W) depending on the state that the data were collected in. The data for each compound were averaged across all sites within that geographic region, and then multiplied by their respective MIR value to give the reactivity adjusted average concentration for that region. Each compound was then scored based on a proportional weighting for each geographic region. The maximum score for each compound over all of the geographic regions was then used for the score for that compound for this factor. Figure 4 summarizes reactivity adjusted average concentrations for the target compounds in each of the regions reviewed.

Secondary Organic Aerosol Precursor

Several of the existing PAMS target compounds are also important secondary organic aerosol precursors (SOAP). This factor was added to account for the added benefit to the air quality program of measuring these SOAP compounds in the PAMS program. A list of the 18 most important SOAP compounds was obtained from the literature (Derwent, 2010). This list was cross referenced versus the PAMS target list, and those PAMS target compounds on the SOAP list were given an additional 5 percent to their final score for this factor. Table 2 lists the PAMS target compounds that were identified as SOAP compounds.

Hazardous Air Pollutants

Several of the existing PAMS target compounds are also hazardous air pollutants. This factor was added to account for the added benefit to the air quality program of measuring these HAP compounds in the PAMS program. The HAP list was cross referenced versus the PAMS target list, and those PAMS target compounds identified as HAP were given an additional 5 percent to their final score for this factor. Table 3 lists the PAMS target compounds that were identified as HAP.

Summary of Results and Selection of Priority Compounds

Figure 1 summarizes the overall score and ranking of the existing target compounds, with the most important compounds on the left with decreasing importance moving to the right. As can be seen, many of the existing compounds have very low importance based on this scoring approach. However, this approach does not by itself identify a “cut point” to separate priority compounds from optional compounds. In order to identify a point to separate the compounds into priority and optional lists, a running sum of the individual scores of each compound was created for each compound. The running sum was made up of the target compound’s score plus the score of all higher ranked compounds. For example, the running sum for ethylene is the sum of the score for ethylene plus the scores for

formaldehyde and isobutane. The running sum for the least important compound includes the scores for all compounds, and is referred to here as the “total value.” By dividing the running sum for a given compound by the total value and multiplying by 100, you obtain an estimate of the percent of the total value obtained by measuring that compound and all higher ranked compounds.

Figure 5 graphically represents this calculation for all current target compounds. As can be seen, a point is reached where measuring each additional compound adds little value. A decision to obtain 90 percent of the value would lead to a cut point between p-ethyltoluene and o-ethyltoluene. The cut point between the priority list and the optional target list was selected after o-ethyltoluene to avoid cutting the lists between these two isomers. In addition, cis-2-butene was included in the priority list to avoid separating it from its isomer trans-2-butene. Table 1 provides the revised priority and optional target lists.

CONSIDERATION OF COMPOUNDS TO ADD

Three considerations were made in evaluating if additional compounds (compounds not currently on the PAMS target list) should be added:

1. If any VOC compounds important to ozone formation were not included in the original target list,
2. If any VOC compounds important to air toxic risks or secondary organic aerosols (SOA) formation were not included in the original target list, and
3. If the existing measurement technologies being used at PAMS sites are capable of measuring the candidate VOC compound.

With respect to important ozone forming VOC compounds that are not included, we note that biogenics have been identified as important to ozone formation (especially in the east) (Samet, 2011). However, isoprene is the only biogenic on the target list. Alpha and beta pinene have also been identified as important biogenic compounds for ozone formation. The existing gas chromatographs (GC) used in the PAMS program are capable of measuring both alpha and beta pinene; however, concerns have been raised about the methods capability of accurately differentiating between alpha and beta pinene. This issue has been addressed before with other VOC isomers, such as m-xylene and p-xylene where separation of the two isomers is difficult. As with m/p-xylene, alpha and beta pinene can be measured and the total be reported as α/β -pinene. As such, α/β -pinene is being added to the priority compound list.

In addition to biogenics, the CASAC monitoring subcommittee also suggested measuring ethanol as a marker for biofuel usage. The use of biofuels has been increasing in recent years, and measuring ethanol will allow for tracking the potential impact on ozone formation due to changes in fuel usage. As such, ethanol is being added to the priority compound target list.

For air toxics, the 2005 NATA (EPA, 2011) was reviewed in order to identify air toxic compounds considered to be either national cancer risk drivers or contributors. Six compounds were identified as national cancer risk drivers or contributors that can be measured using the existing measurement technologies, including - 1,3 butadiene, acrylonitrile, carbon tetrachloride, ethylene oxide, tetrachloroethylene, and 1,4-dichlorobenzene. Of these six compounds, the National Air Toxics Trends Sites (NATTS) program currently measures 1,3 butadiene, carbon tetrachloride, and tetrachloroethylene. For consistency with the NATTS, these three compounds are being added to the priority compound target list.

The list of SOA compounds discussed above was reviewed again to identify if any compounds should be considered for addition to the target list. Only benzaldehyde was identified as a compound that was considered an important SOA but that was not on the current target list. Benzaldehyde can be measured along with the other carbonyls currently on the target list (formaldehyde, acetaldehyde, and acetone). As such, benzaldehyde is being added to the priority compound target list.

IMPLEMENTATION OF LIST CHANGES

Based on this guidance, PAMS monitoring agencies should focus their reporting on the existing priority compounds listed in Table 1 beginning in the 2014 PAMS season. Continued reporting of the optional compounds may continue on a voluntary basis but should be reviewed in the overall context of agency reporting burdens.

The EPA is evaluating the ability of the existing equipment to measure the new priority compounds listed in Table 1. These compounds will be evaluated as part of an auto-GC evaluation currently planned for the winter of 2013 and the EPA will be soliciting volunteers from state and local monitoring agencies to assist in the evaluation during the 2014 PAMS season. In addition, the current PAMS retention time cylinders do not include the new priority compounds, which would make it more difficult for monitoring agencies to identify the peaks for the new priority compounds. As such, monitoring agencies should wait until the 2015 PAMS monitoring season to begin measuring and reporting the new priority compounds listed in Table 1, by which time EPA will have completed the review of the new compounds and appropriate retention time cylinders are available.

Table 1 lists four carbonyl compounds as priority compounds. It should be noted that under the current regulatory requirements for PAMS, carbonyls are only required to be measured at PAMS areas classified as severe and above nonattainment areas for ozone. This guidance does not supersede the regulatory requirements. However, due to the importance of carbonyl measurements in understanding ozone formation, PAMS monitoring agencies are encouraged to consider measuring carbonyls at their PAMS sites.

REFERENCES

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Attachments

Table 1. Revised PAMS Target List

Existing Priority Compounds	Optional Compounds
1,2,3-Trimethylbenzene	1,3,5-Trimethylbenzene
1,2,4-Trimethylbenzene	1-Pentene
1-Butene	2,2-Dimethylbutane
2,2,4-Trimethylpentane	2,3,4-Trimethylpentane
Acetaldehyde ^a	2,3-Dimethylbutane
Acetone ^a	2,3-Dimethylpentane
Benzene	2,4-Dimethylpentane
Cis-2-Butene	2-Methylheptane
Ethane	2-Methylhexane
Ethylbenzene	2-Methylpentane
Ethylene	3-Methylheptane
Formaldehyde ^a	3-Methylhexane
Isobutane	3-Methylpentane
Isopentane	Acetylene
Isoprene	Cis-2-Pentene
M/P Xylene	Cyclohexane
M-Ethyltoluene	Cyclopentane
N-Butane	Isopropylbenzene
N-Hexane	M-Diethylbenzene
N-Pentane	Methylcyclohexane
O-Ethyltoluene	Methylcyclopentane
O-Xylene	N-Decane
P-Ethyltoluene	N-Heptane
Propane	N-Nonane
Propylene	N-Octane
Styrene	N-Propylbenzene
Toluene	N-Undecane
Trans-2-Butene	P-Diethylbenzene
	Trans-2-Pentene
New Priority Compounds	
α/β -Pinene	
1,3 Butadiene	
Benzaldehyde ^a	
Carbon Tetrachloride	
Ethanol	
Tetrachloroethylene	

^a These compounds are carbonyls and are only required to be measured at PAMS sites in ozone nonattainment areas classified as severe or extreme.

Table 2. PAMS Targets that are HAP Compounds

2,2,4-Trimethylpentane
Acetaldehyde
Benzene
Ethylbenzene
Formaldehyde
Isopropylbenzene
M/P Xylene
N-Hexane
O-Xylene
Styrene
Toluene

Table 3. PAMS Targets Identified as Important SOAP Compounds

1,2,3-Trimethylbenzene
1,2,4-Trimethylbenzene
Benzene
Ethylbenzene
M/P Xylene
M-Ethyltoluene
N-Propylbenzene
O-Ethyltoluene
O-Xylene
P-Ethyltoluene
Styrene
Toluene

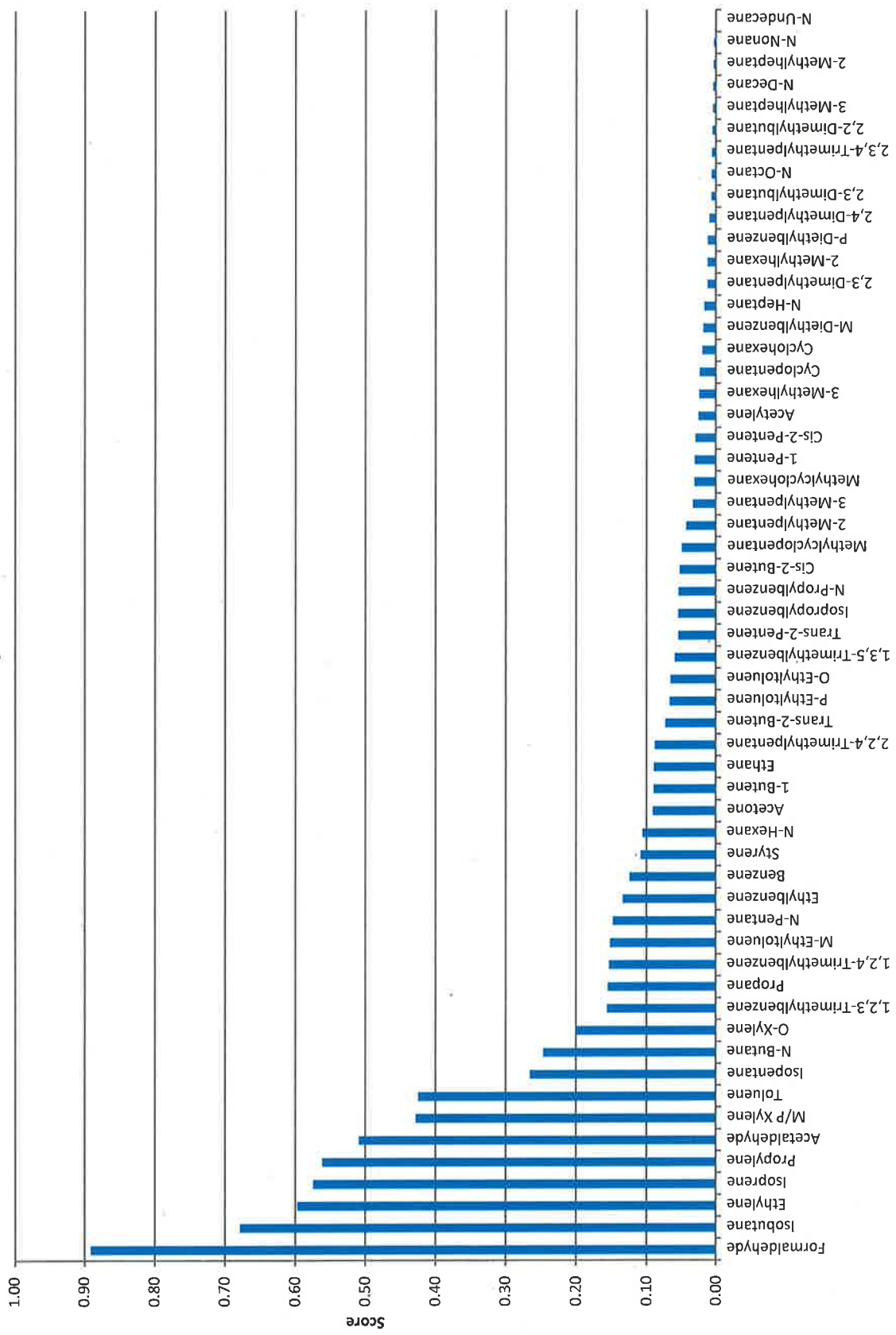


Figure 1. Overall Ranking of PAMS Targets Based on Decision Matrix Scoring

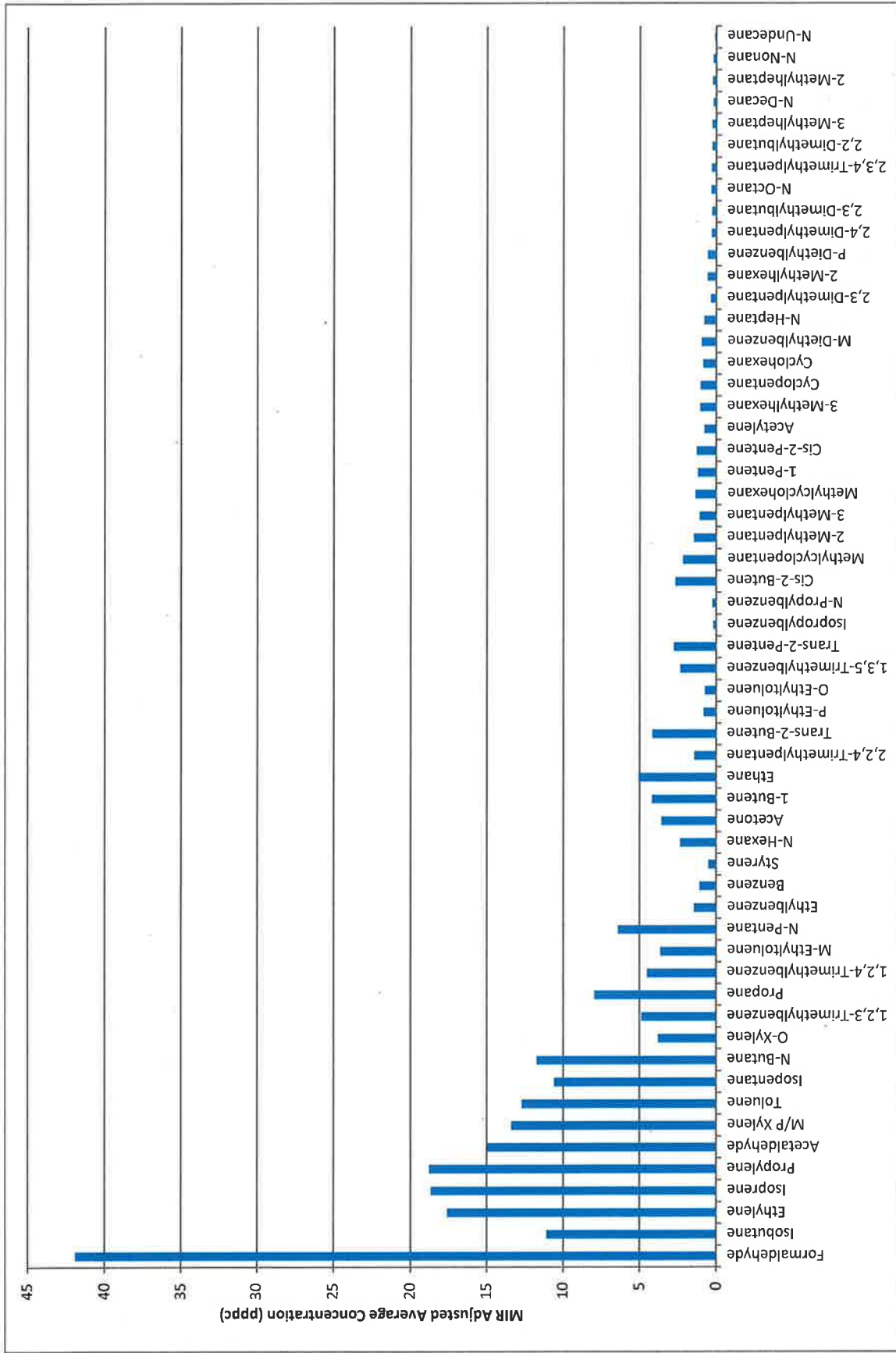


Figure 2. Summary of Overall Average MIR Adjusted Concentration

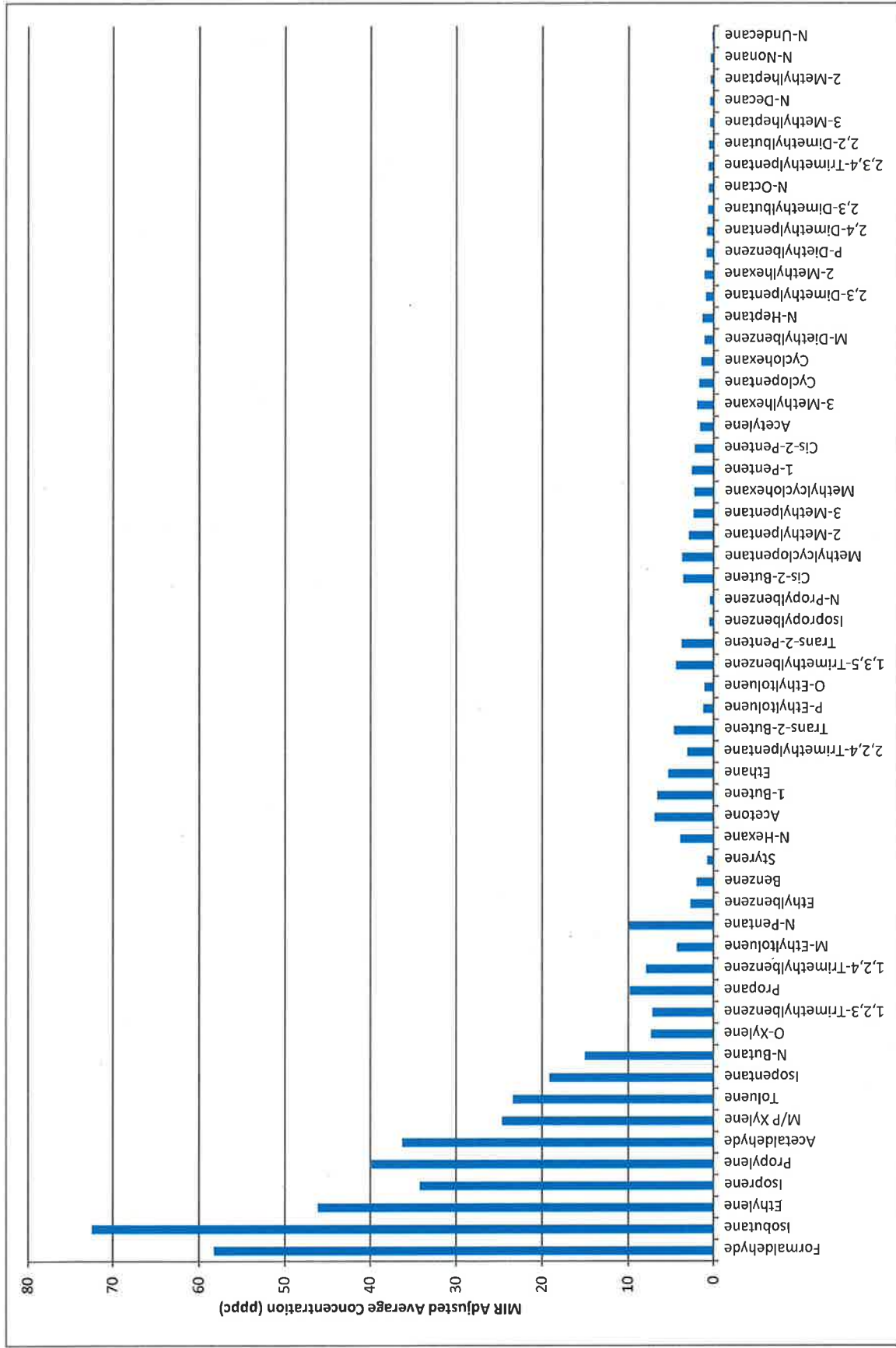


Figure 3. Summary of MIR Adjusted Average Concentration During 9 am Hour on High Ozone Days

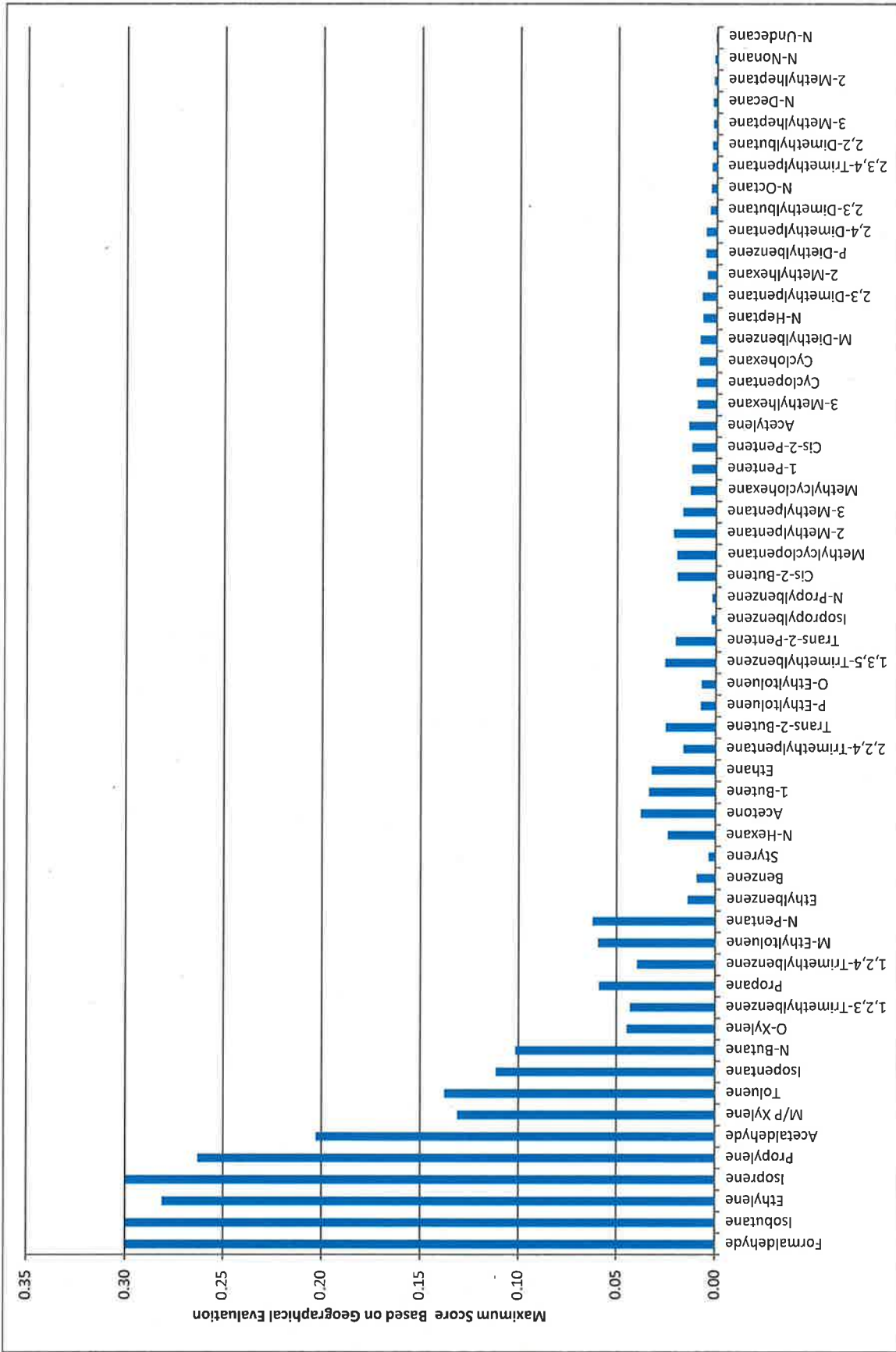


Figure 4. Summary of Scores for MIR Adjusted Average Concentration Based on Geographic Location

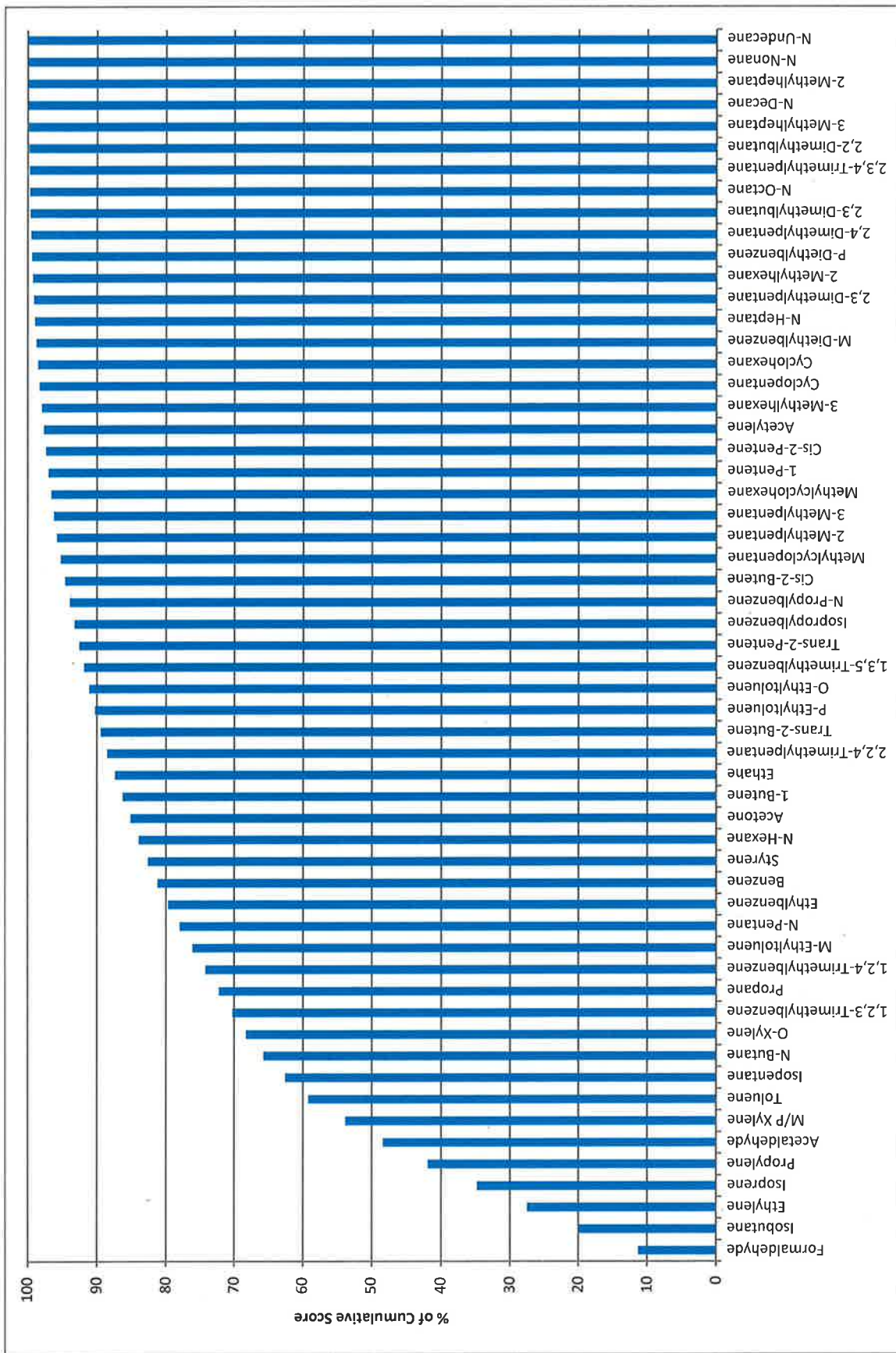


Figure 5. Summary of Running Sum of Individual Scores