Use of PIANO data to Identify source and potential age of subsurface LNAPL at a pipeline terminal

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Site History and Project Objective

Pipeline Terminal Site

Floating product found in a site monitoring well.

Report provided to client identifying a low-octane gasoline product type

Second floating product collected from the same well one year later.

Objective:

Full characterization of Year 1 sample to assist in determining likely source.

- Compare to Year 2 sample and to several reference products
- Evaluate product composition
- Determine if site samples appear to be from the same source
- Estimate degree of weathering/degradation

Samples and Analyses

Analytical Test	Test Description
SHC	Saturated Hydrocarbons: 80-minute GC-FID chromatographic run of free product or a sample extract, reporting n-alkanes and five isoprenoids from n-C9 to n-C40 plus total saturated and petroleum hydrocarbons. Used to characterize the composition and potential degradation state of a middle-distillate or heavier hydrocarbon product.
Whole Oil	GC-FID injection of a diluted product sample. Output is a 120-minute GC-FID chromatogram showing the overall composition from n-C4 to n-C44.
PIANO	Paraffin, isoparaffin, aromatic, naphthenes and olefin composition. Over 120 volatile compounds from these classes plus common oxygenate additives are identified with concentrations reported. Used to characterize light-end refined products such as gasoline or jet fuel.
Ethanol	Used to identify and characterize ethanol blended fuels.
Density	Used to determine if the product falls in the expected range for hydrocarbon product in question.

Specific Gravity

- Year 1 sample has higher density than expected for a gasoline product.
  - Not so high that indicates a non-gasoline source.
- Could be due to degradation:
  - Petroleum products generally increase in density as they degrade.
  - Shorter, lighter components usually degrade faster leaving a higher proportion of heavier components.
- Could be due to a mixed source with some amount of a heavier petroleum product present.

Measured Density = 0.79 g/mL

Typical gasoline range: 0.72-0.78 g/mL

Typical diesel range: 0.75-0.85 g/mL

Oxygenate / Ethanol Analysis

Methyl tertiary butyl ether (MTBE) detected at 400 mg/kg.

No other oxygenated fuel additives were detected.

> e.g. ethyl ether, ethyl tertiary butyl ether, tertiary amyl-methyl ether or tertiary butanol

No ethanol detected in the sample.

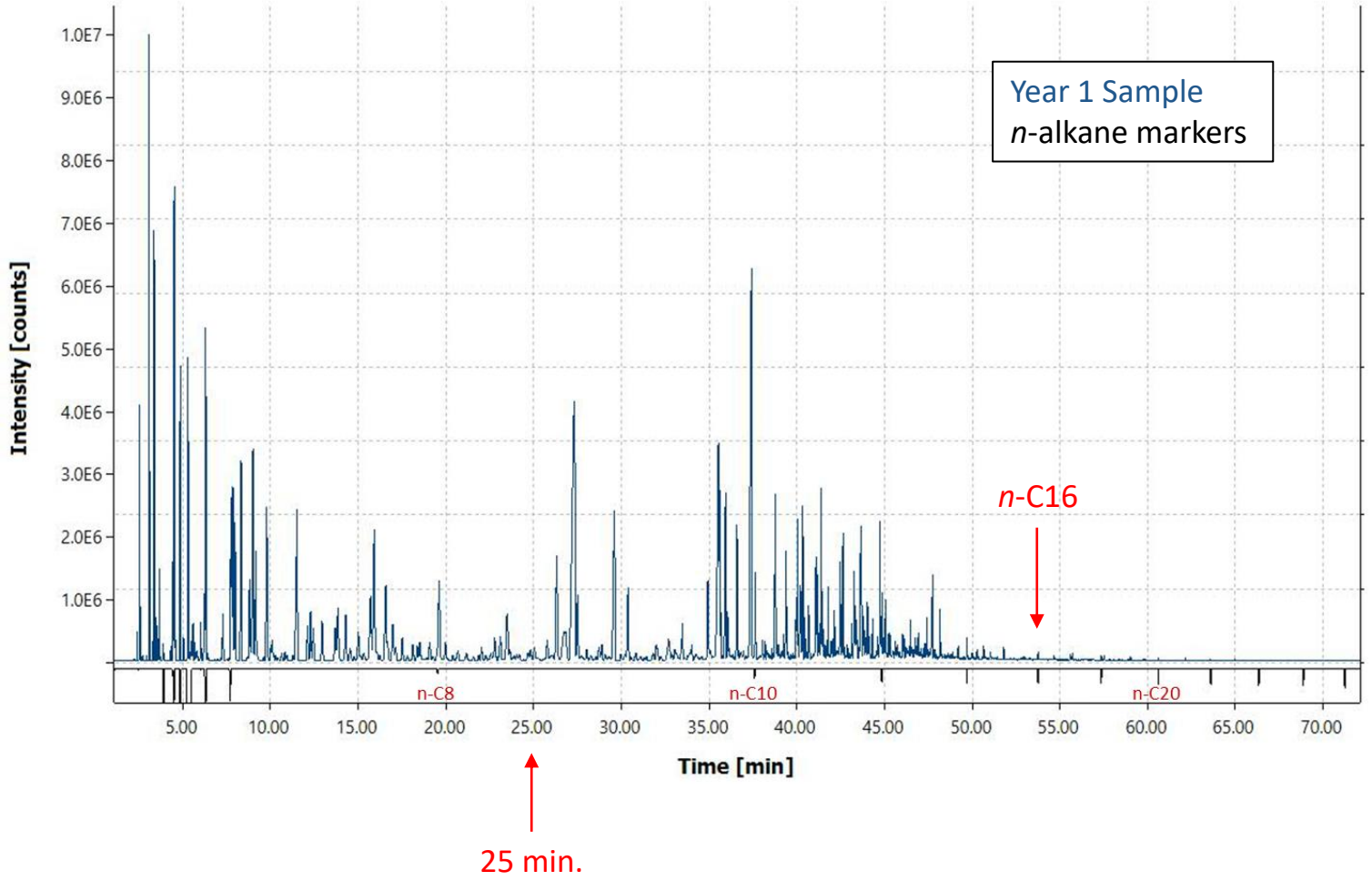
Suggests either a pre-MTBE-ban degraded fuel or a post ban non-blended fuel.

MTBE Detection

- MTBE presence may infer of a fuel produced prior to the 2005-2006 elimination of MTBE in automotive fuels, but not conclusive.
- Often found in post-ban gasolines to account for unintentional cross contamination in the supply chain. A recent report* demonstrated:
  - 34% of fuels collected post-ban had MTBE at 290 ± 307 mg/kg.
  - 61% of pre-ban gasolines tested contained MBTE at 11,800 ± 16,500 mg/kg.
- MTBE can biodegrade to t-butyl alcohol (TBA) in reducing environments.
  - Reported half-lives of 1.6 yr to 5.8 yr
- MTBE could have arisen from a pre-2006 source either due to degradation or a high dilution of a more recent gasoline product.

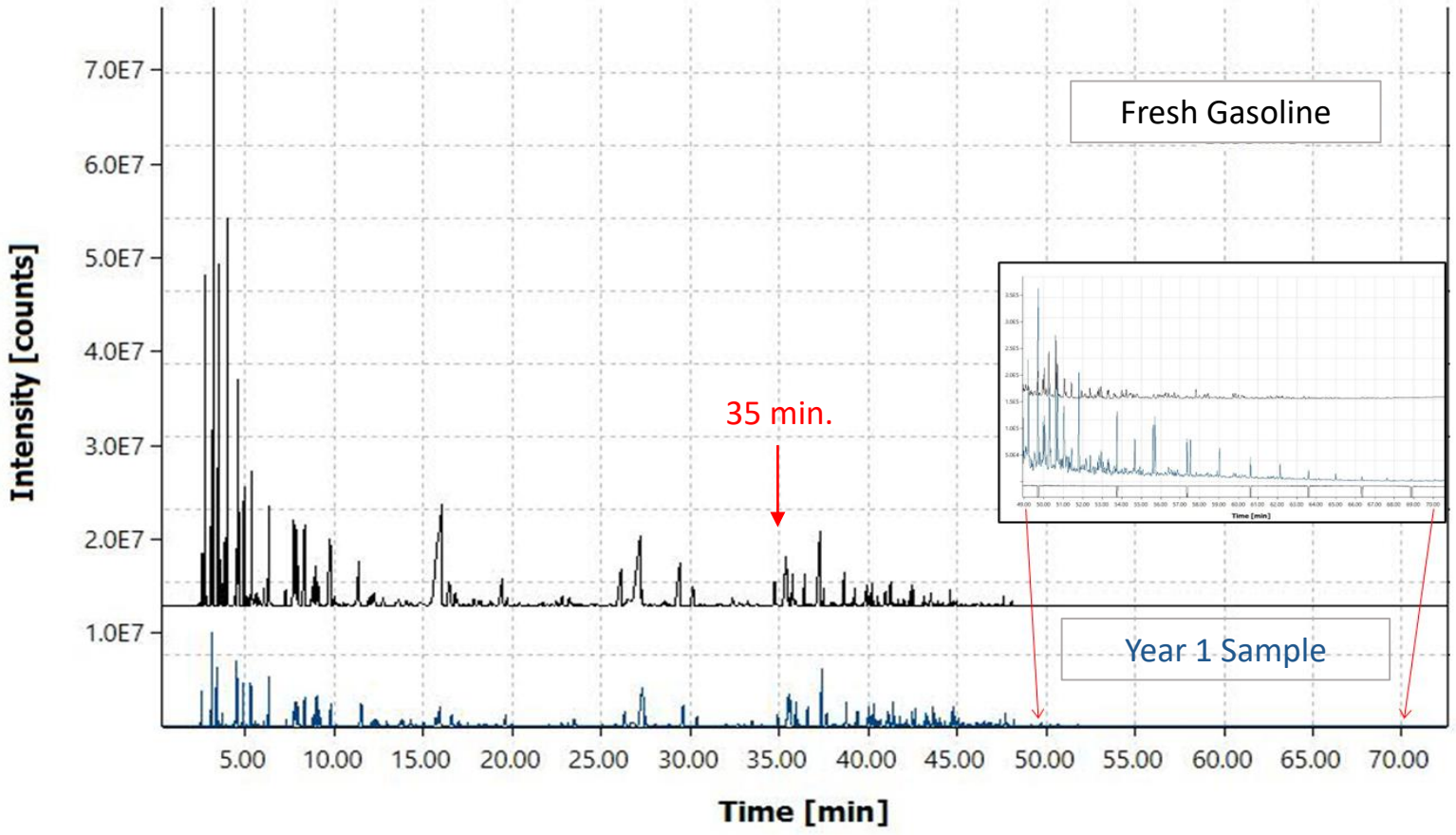
*Stout, S.A. and E. Healey. Environmental Forensics. DOI: 10.1080/15275922.2023.2218293.

Whole Oil Analysis – Year 1 Sample



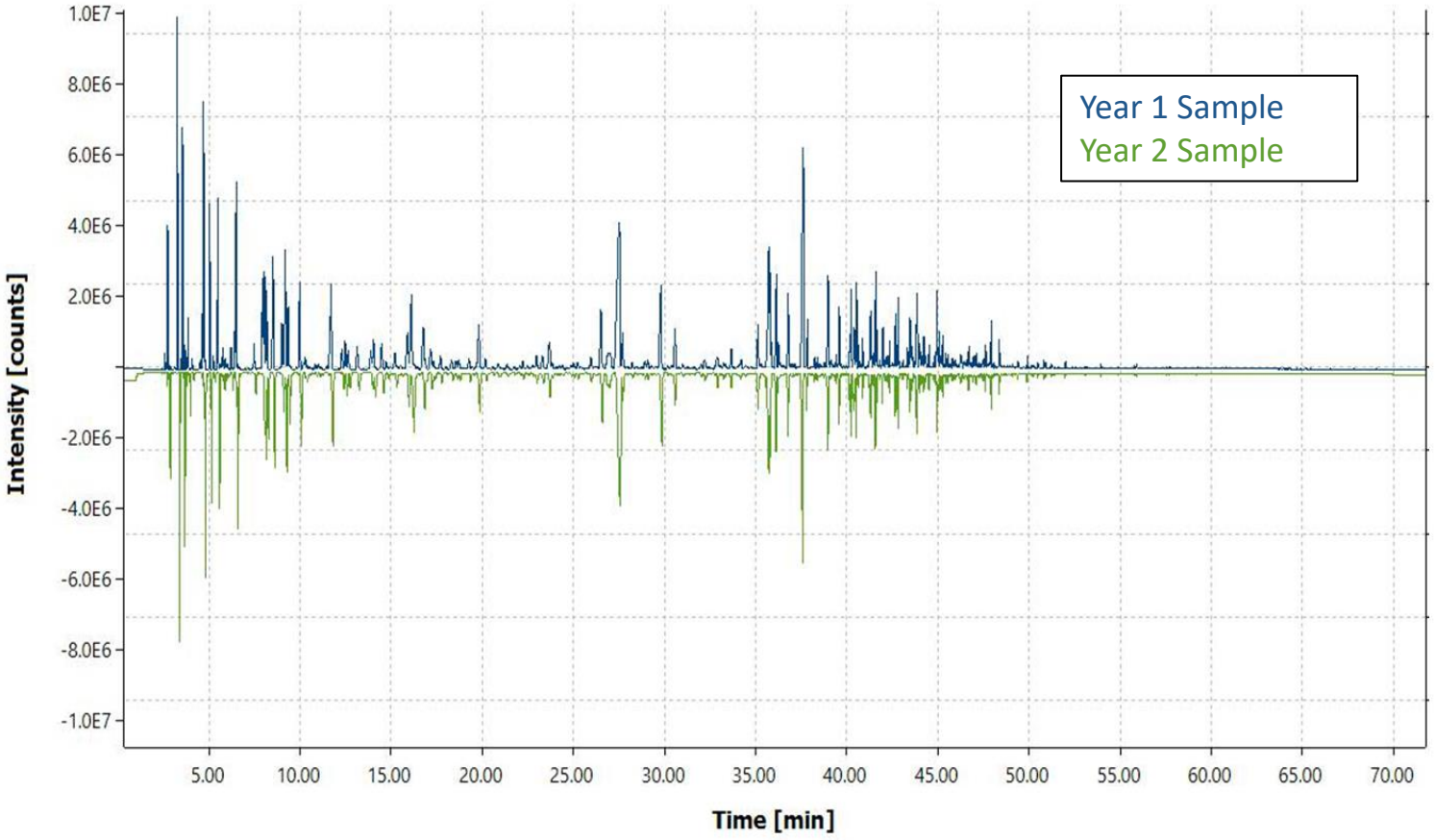
- Sample contains hydrocarbons in the gasoline and kerosene ranges (i.e., ≤ *n*-C16).
- Peak heights <25 min in Year 1 sample, seem lower than expected for a fresh gasoline.

Whole Oil Analysis – Year 1 Sample vs. Fresh Gasoline



- Many peaks <35 min. have heights 10% - 90% of those in the fresh gasoline.
  - Suggests degradation in the lower boiling point components.
  - e.g. water washing, volatilization, microbial action.
- Several small peaks are seen after ~48 min (> *n*-C14), extending to at least 70 minutes (n-C26).
  - Not expected in gasolines.

Whole Oil Analysis – Year 1 vs Year 2



- Very little difference in the profiles.
- Component peak heights, i.e. concentrations – nearly identical >6 min.
- 10% to 30% drop in peak heights <6 min. suggests minimal degradation over 1 yr.

SHC Analysis – Year 1 Sample

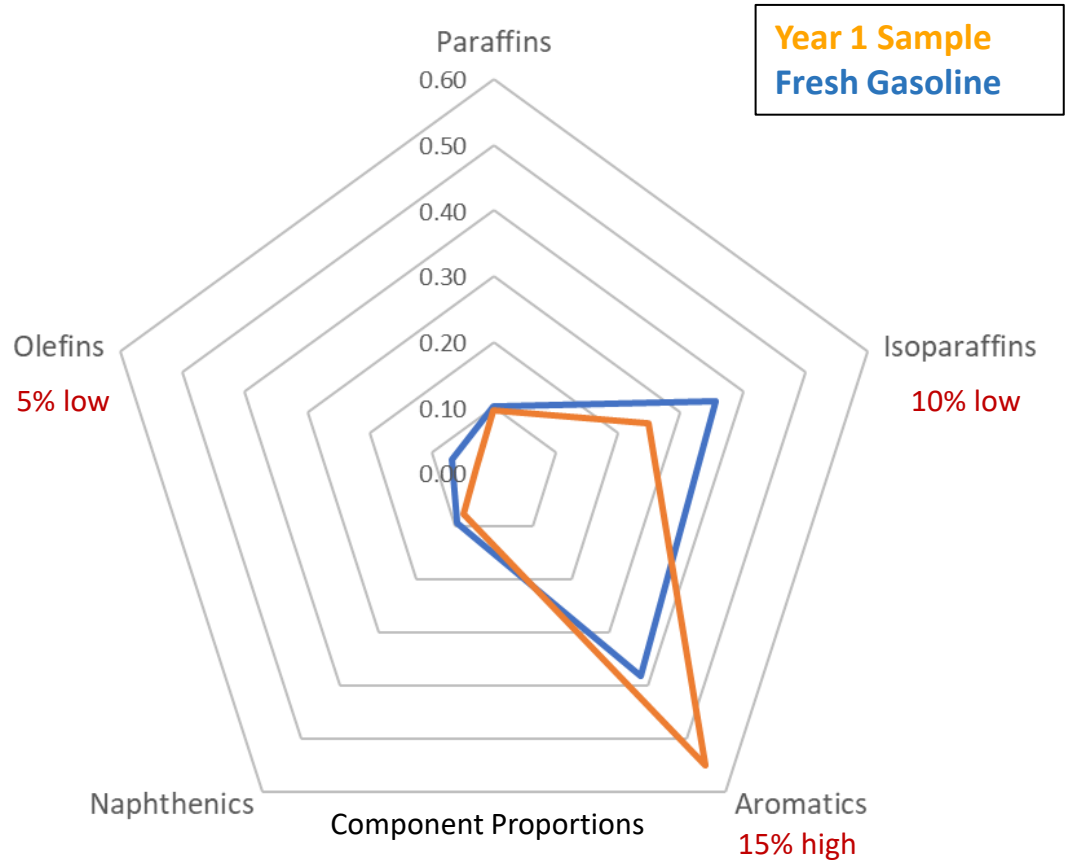
Analyte	Concentration (mg/kg)	Ratios
***n*-C14**	1410	--
***n*-C15**	687	--
***n*-C16**	413	--
nor-Pristane	266	--
***n*-C17**	308	n-C17/Pr = 0.69
Pristane	448	
***n*-C18**	231	n-C18/Py = 0.86
Phytane	268	

Saturated hydrocarbons detected from *n*-C9 to *n*-C23.

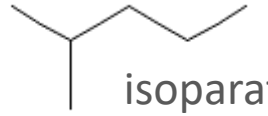
- SHC present at 6% of Total Petroleum Hydrocarbon.
  - Suggests a refined product.
- Saturated hydrocarbons >n-C16 provides additional evidence that the sample contains some higher boiling range product.
- *n*-alkane to isoprenoid ratios < 1 suggest that the higher boiling point component may be at a more advanced degradation stage.

PIANO Analysis

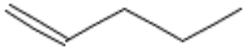
Profile of 142 analytes classified as paraffinic, isoparaffinic, aromatic, naphthenic or olefinic



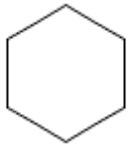
paraffin



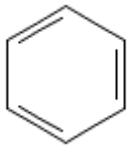
isoparaffin



olefin

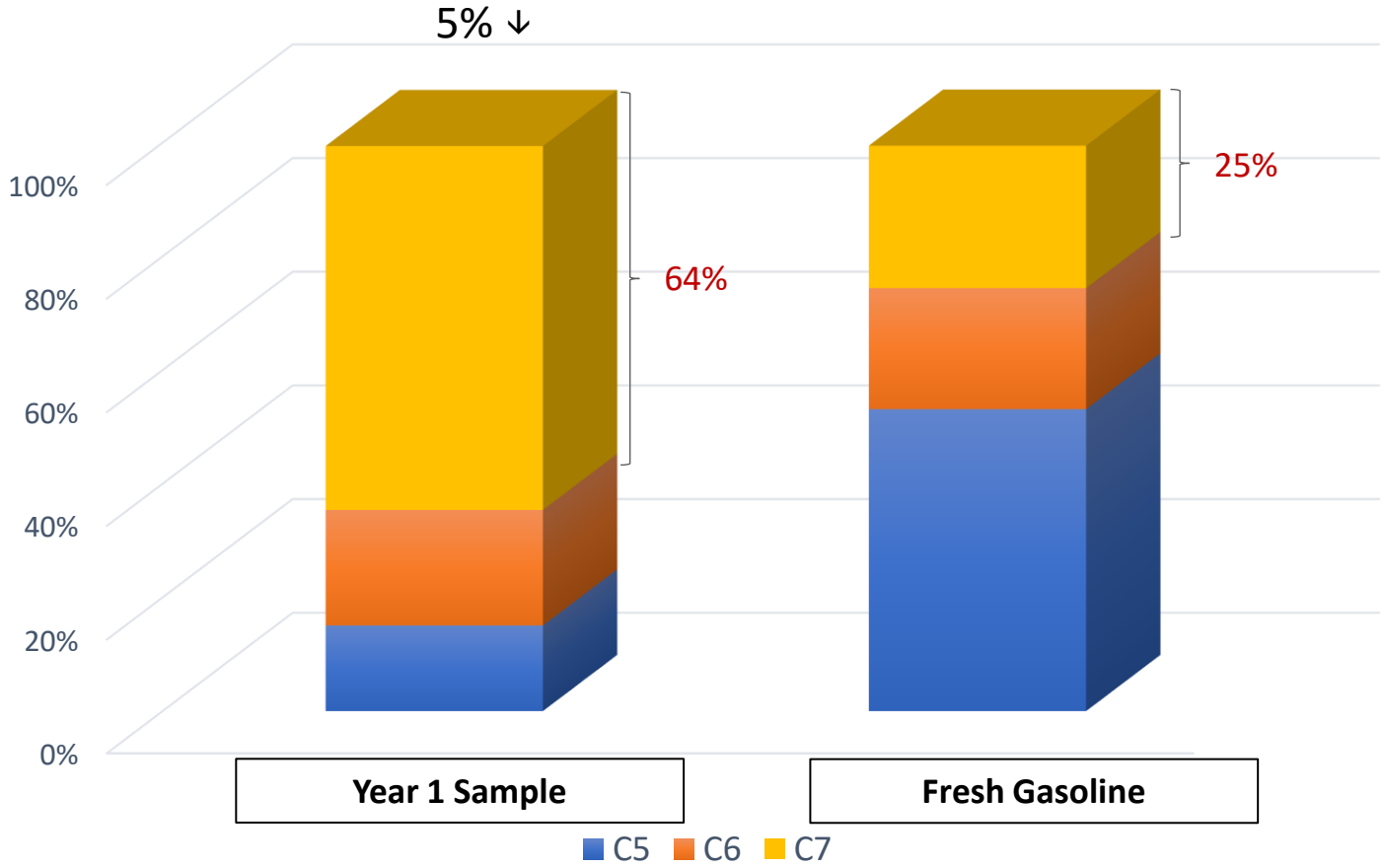


naphthene



aromatic

PIANO Analysis - Olefins

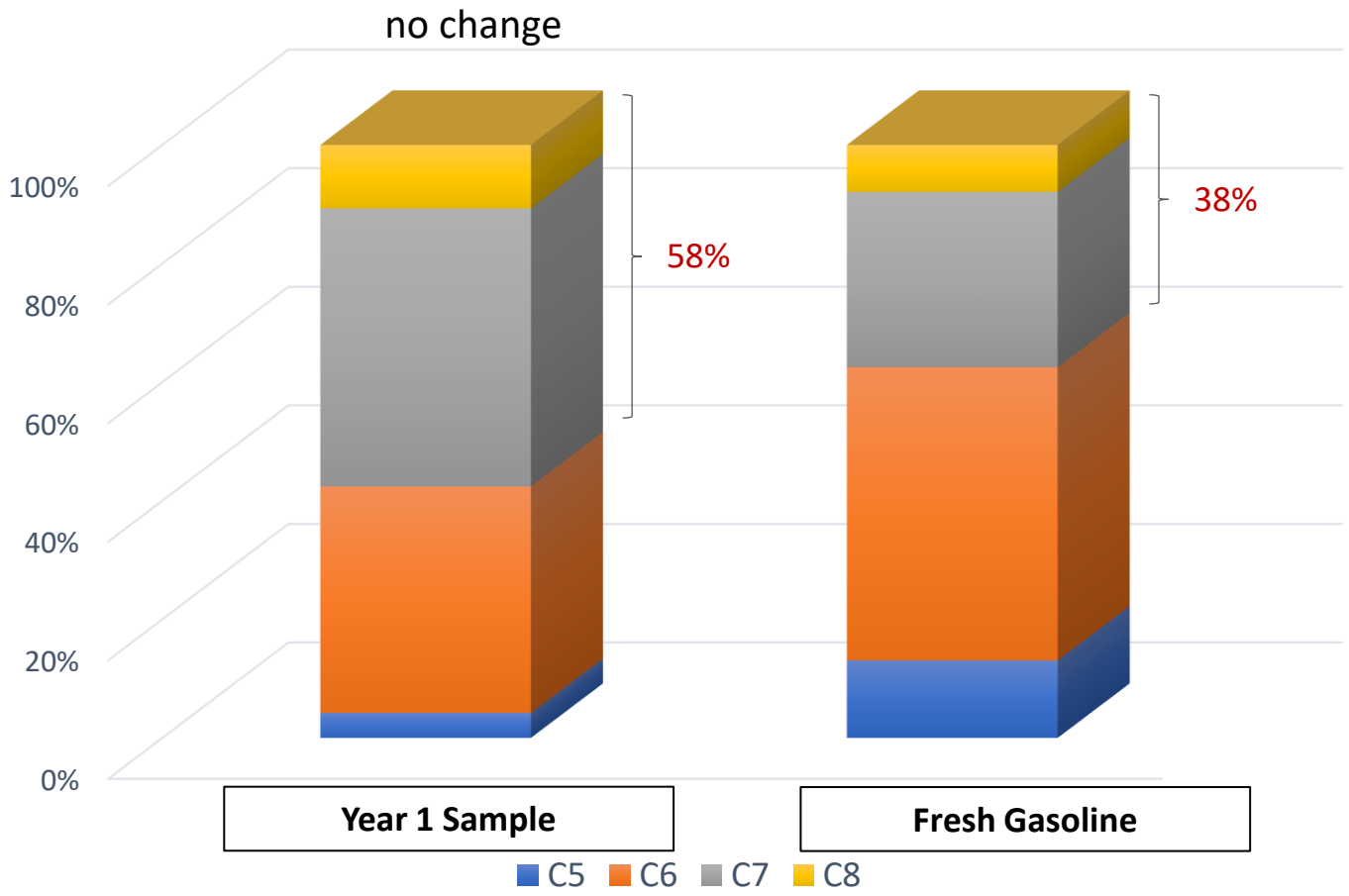


Bands on each bar represent olefins with progressively higher numbers of carbons.

Higher bars represent greater recalcitrance.

Year 1 sample is dominated by the more recalcitrant olefins.

PIANO Analysis - Naphthenes

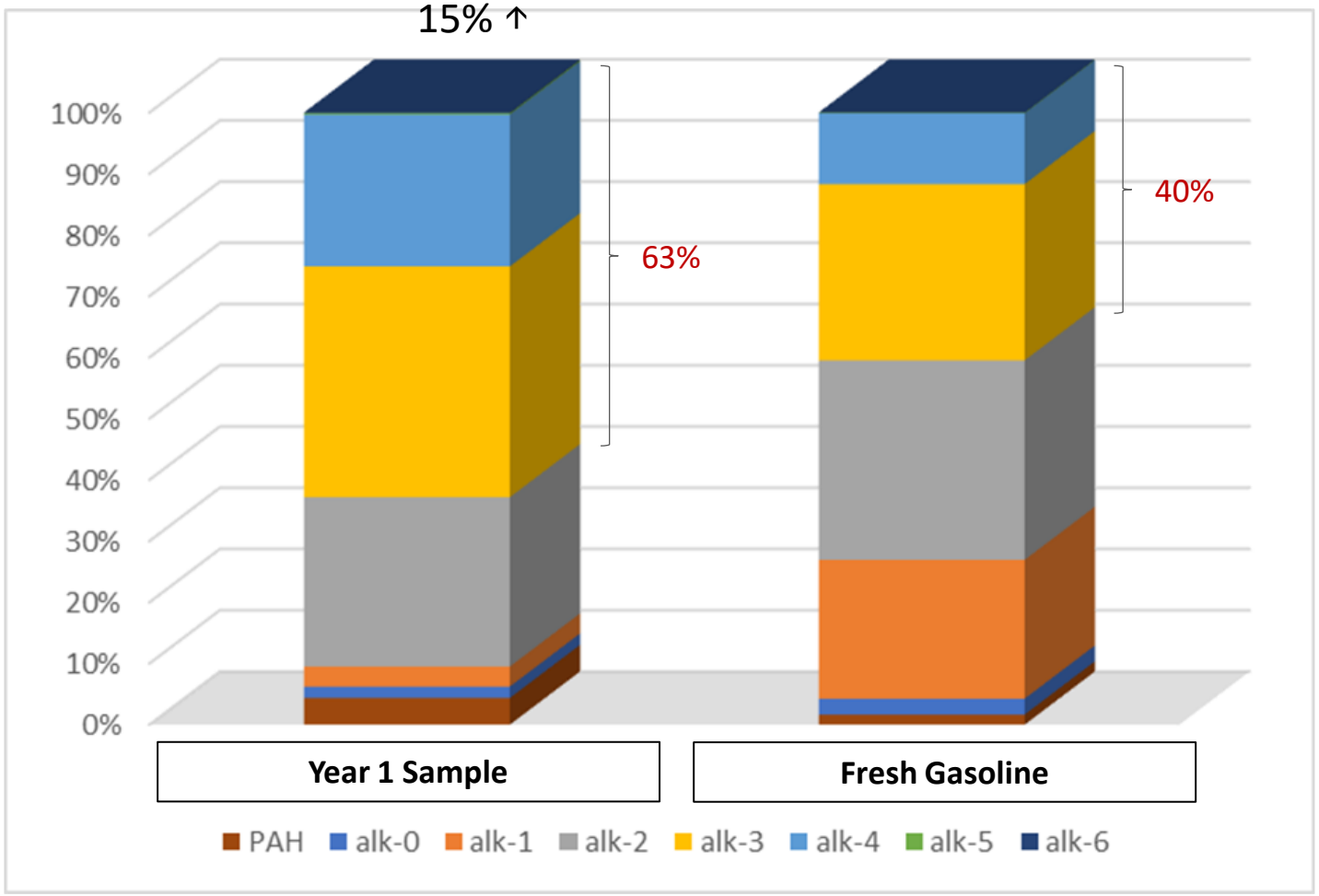


Bands on each bar represent naphthenes with progressively higher numbers of carbons.

Higher bars represent greater recalcitrance.

Year 1 sample is dominated by the more recalcitrant naphthenes.

PIANO Analysis - Aromatics



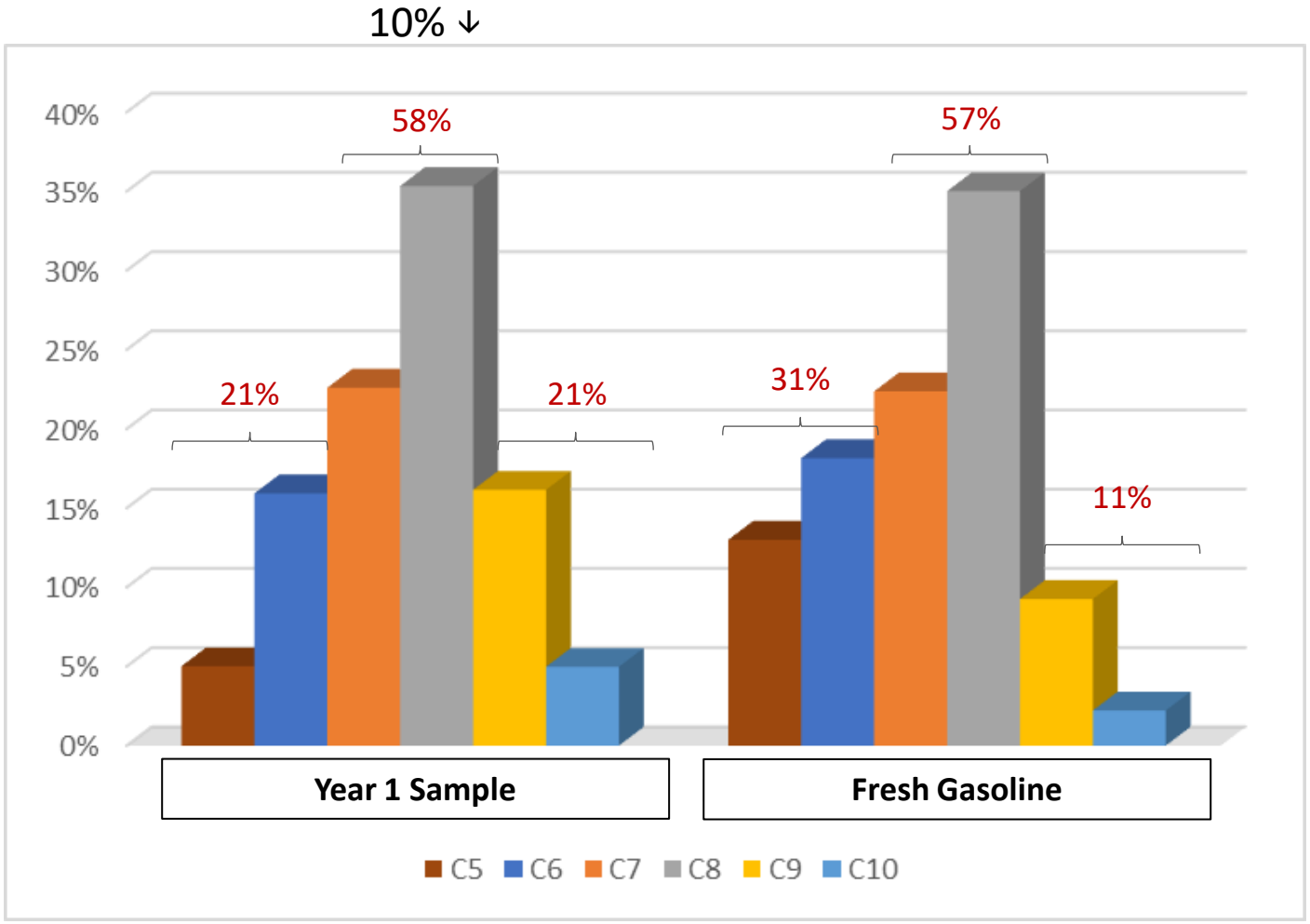
Overall aromatic composition for both samples is > 95% alkylbenzenes with the remainder being PAHs.

Bands on each bar above PAH represent alkylbenzenes with progressively higher degrees of alkylation.

Above PAH, higher bars represent greater recalcitrance.

Year 1 sample is dominated by the more recalcitrant alkyl benzenes.

PIANO Analysis - Isoparaffins



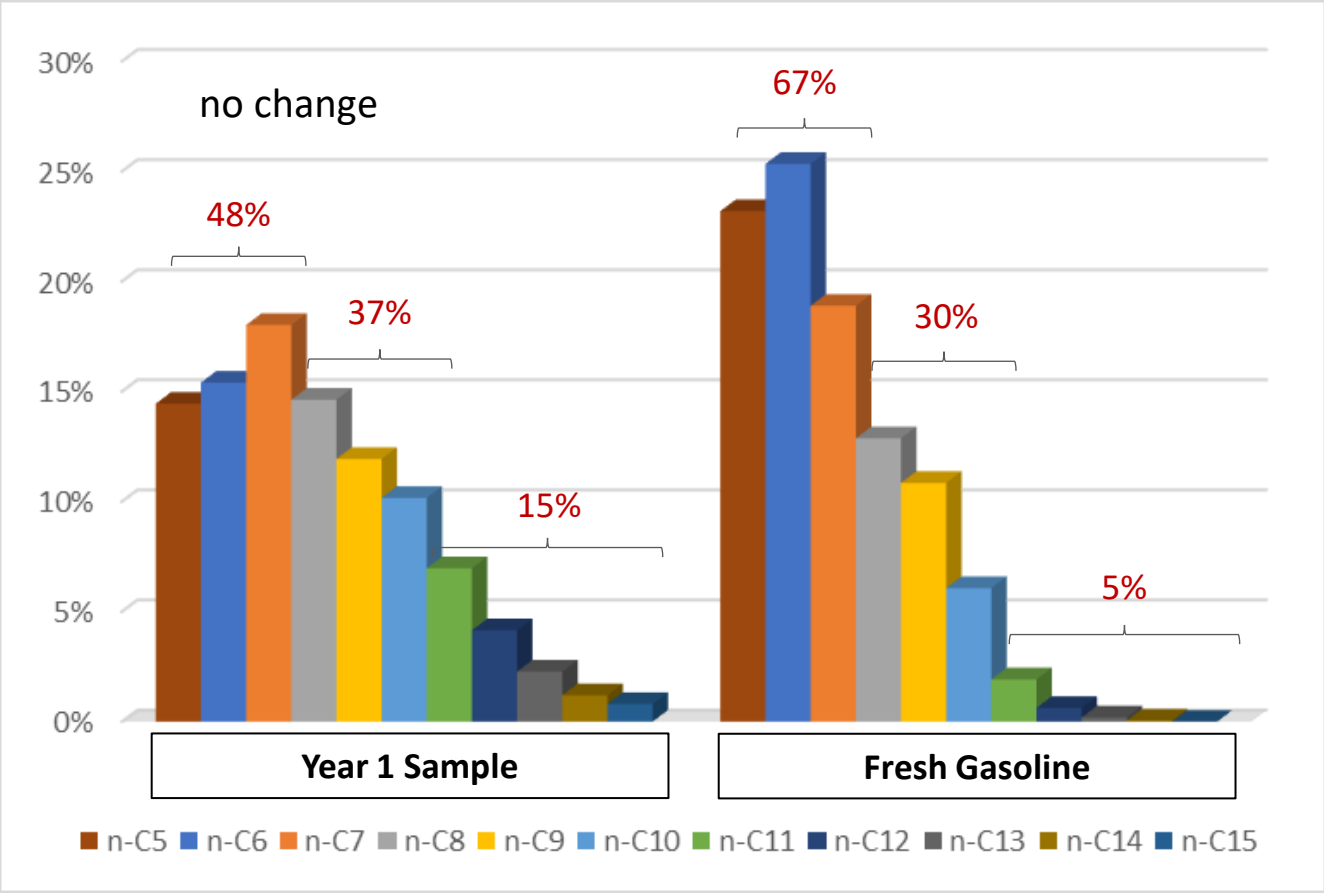
Bars represent groups of branched alkanes having equivalent total carbon numbers.

Isoparaffins with progressively higher total carbon numbers roughly correlates with increasing recalcitrance.

Year 1 Sample has 10% less of C5-C6 and 10% more C9-C10.

i.e. preferential degradation of short isoparaffins.

PIANO Analysis - Paraffins



19% drop in *n*-C5 to *n*-C7 comparable to the 17% increase in *n*-C8 to *n*-C15

Overall paraffins proportions were equivalent, but...

Distribution suggests degradation in short-chain paraffins.

Data Interpretation

The product samples appear to originate from the same source.

The source is most likely comprised of two components:

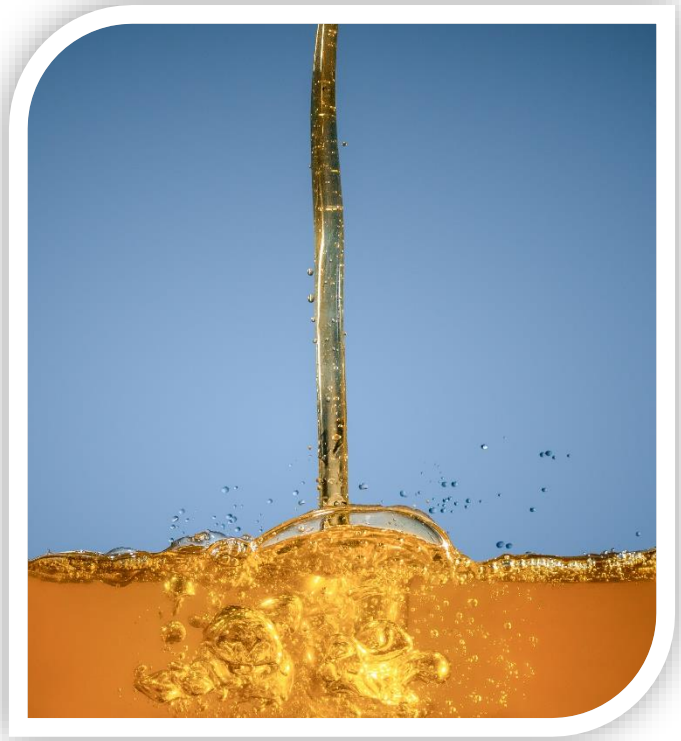
- Dominated by a gasoline range hydrocarbon product at a moderate to advanced degree of degradation.
- A minor component of an older more highly degraded middle distillate product extending through the diesel range:
  n-C16 to n-C26

Multiple lines of evidence suggest significant degradation in the gasoline component:

- Higher than expected density.
- SHC with reduced concentrations of early eluting peaks relative to the reference fresh gasoline.
- Loss of less recalcitrant components in all five PIANO classes.

Key Take-Aways

- Gasoline degradation may or may not cause a change in the PIANO class proportions.
- Preferential degradation of the less recalcitrant, more volatile or water-soluble components may cause a shift in the distribution of compounds within a class.
- Reduced levels of the more recalcitrant components of all PIANO classes strongly suggests degradation rather than normal variability from one refinery to another.



Thank You!

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