

Modeling Petroleum Hydrocarbon Degradation. Part I, Gasoline. Statistics and Pattern Assemblage.

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Hydrocarbon degradation statistics

Once released to the environment, petroleum hydrocarbons are not stable. That is, they undergo chemical changes consistent with their surroundings and their chemical structure. The changes that take place can be described in a variety of ways.

The overall effects of individual reactions that change individual hydrocarbons have come to be known collectively as “petroleum weathering.”

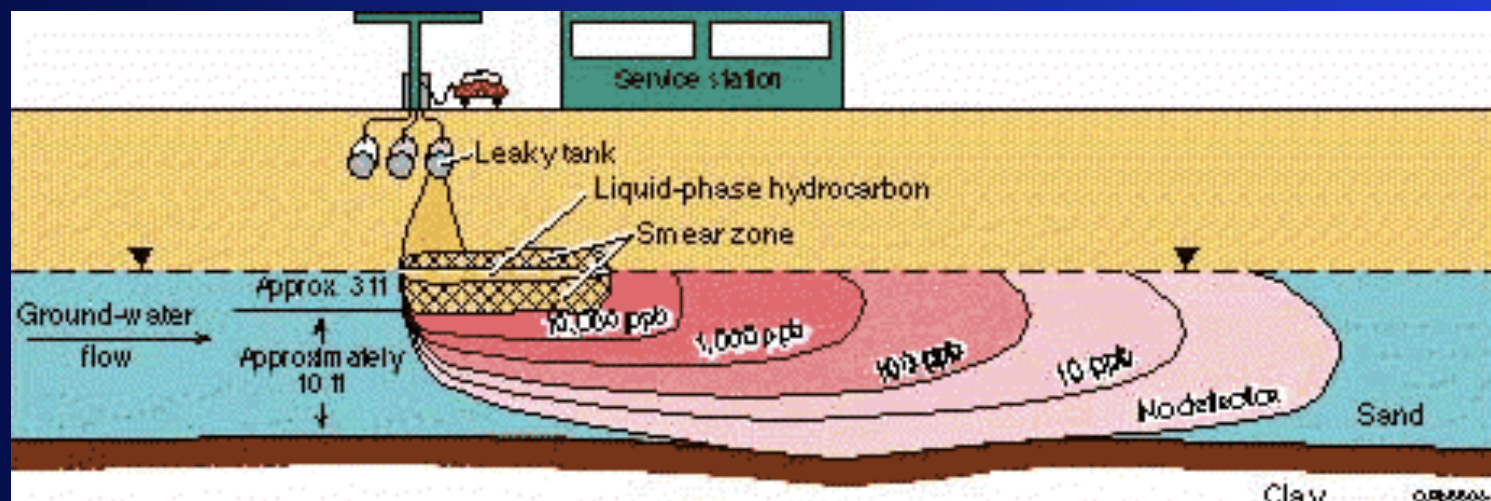
Hydrocarbon degradation statistics

Here is the problem:



Hydrocarbon degradation statistics

A leak from an underground gasoline storage tank releases a single product which first saturates the adjacent soils and then migrates into groundwater. Following the groundwater gradient . . .



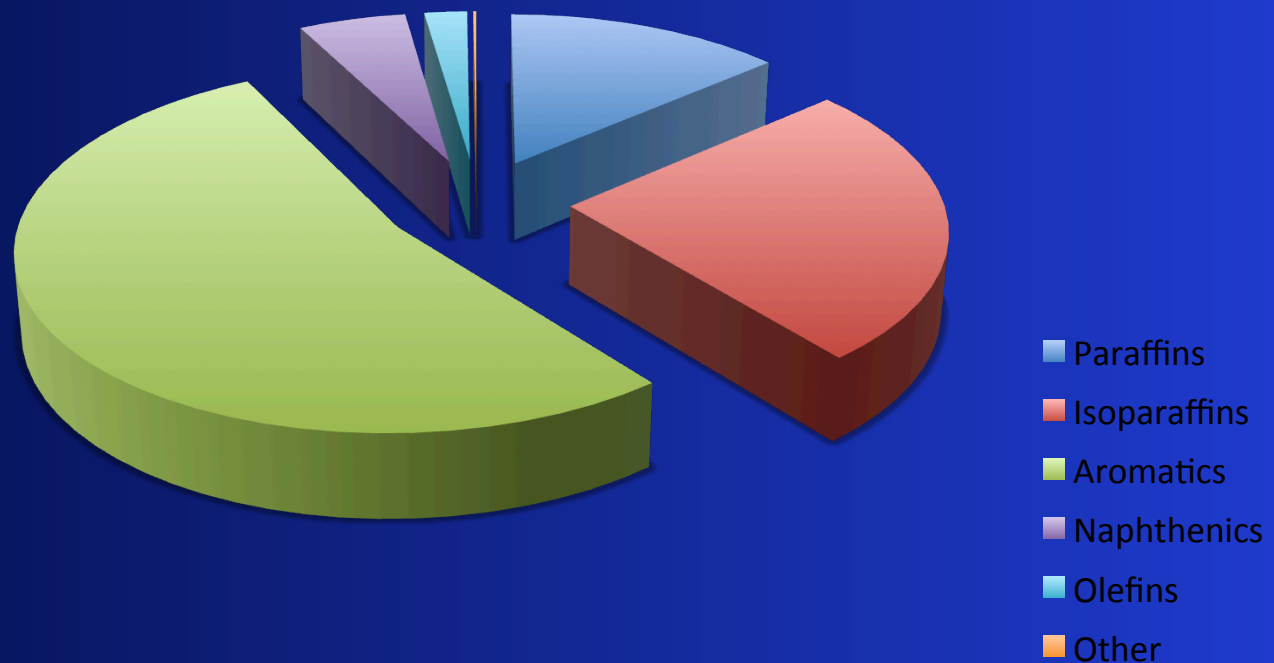
Hydrocarbon degradation statistics

We can collect samples of original fuels, and impacted soils and/or groundwater, ship them to a high level forensic analytical laboratory and collect a large amount of data.

For gasoline releases, we can follow the five principal hydrocarbon classes of gasoline: paraffins, isoparaffins, aromatics, naphthenics and olefins or the PIANO (or PONA) analyses. Unfortunately, not enough target analyte uniformity yet among labs.

Hydrocarbon degradation statistics

With such data, we can examine each of the five major categories of gasoline HCs and begin to ask questions.



Hydrocarbon degradation statistics

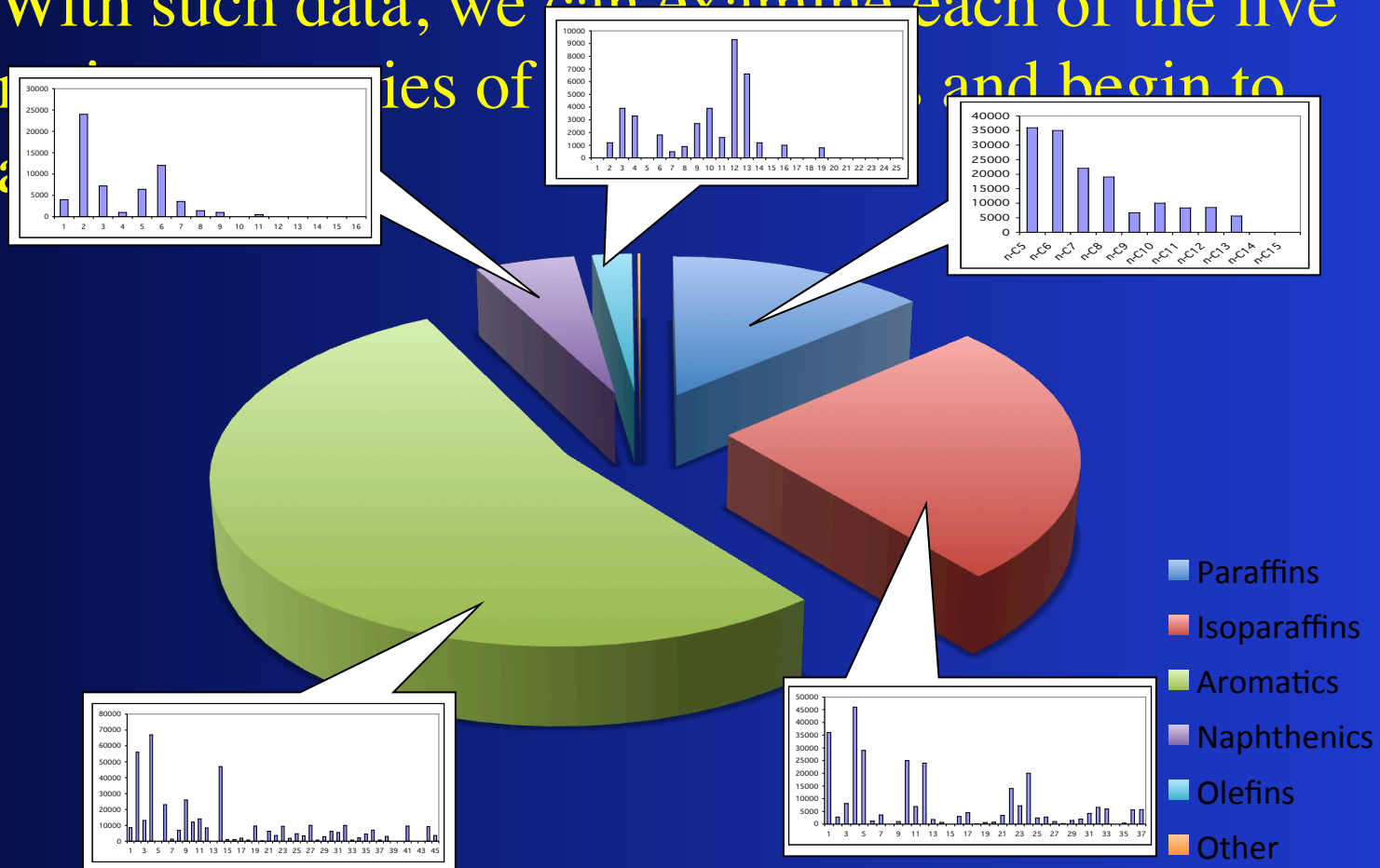
| Fuel Type | Alkane Range | BP Range (°C) |
|----------------------------|--------------|---------------|
| Gasolines (GRO) | | |
| Automotive | C4 - C12 | 50-200 |
| Aviation | C4 - C12 | 25-170 |
| Distillate Fuel Oils (DRO) | | |
| Fuel Oil No. 1 | C9 - C16 | 150-300 |
| Fuel Oil No. 2 | C11 - C20 | 160-360 |
| Residual Fuel Oils (RRO) | | |
| Fuel Oil No. 4, 5, 6 | > C20 | 350-650 |

Hydrocarbon degradation statistics

| Component | Formula | BP (°C) |
|------------------------|---------------------------------------|---------|
| Pentane | $n\text{-C}_5\text{H}_{12}$ | 36 |
| Benzene | C_6H_6 | 80 |
| Toluene | $\text{C}_6\text{H}_5\text{CH}_3$ | 110 |
| Isooctane | C_8H_{18} | 116 |
| Octane | $n\text{-C}_8\text{H}_{18}$ | 126 |
| o-, m-, p-Xylene | $(\text{CH}_3)_2\text{C}_6\text{H}_4$ | 144 |
| Nonane | $n\text{-C}_9\text{H}_{20}$ | 150 |
| Decane | $n\text{-C}_{10}\text{H}_{22}$ | 174 |
| Undecane | $n\text{-C}_{11}\text{H}_{24}$ | 196 |
| 1,2,4-Trimethylbenzene | $(\text{CH}_3)_3\text{C}_6\text{H}_3$ | 176 |
| Pentadecane | $n\text{-C}_{15}\text{H}_{32}$ | 271 |

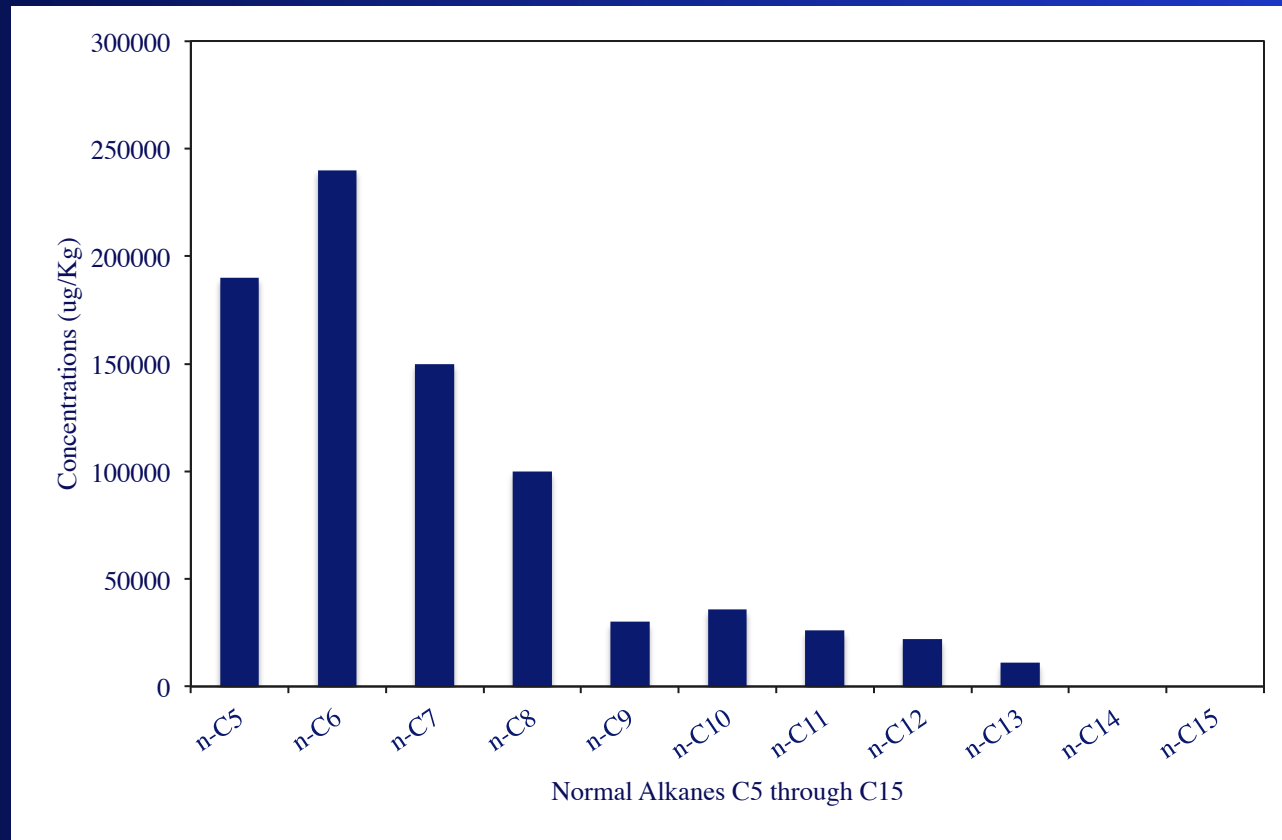
Hydrocarbon degradation statistics

With such data, we can examine each of the five
categories of hydrocarbons and begin to



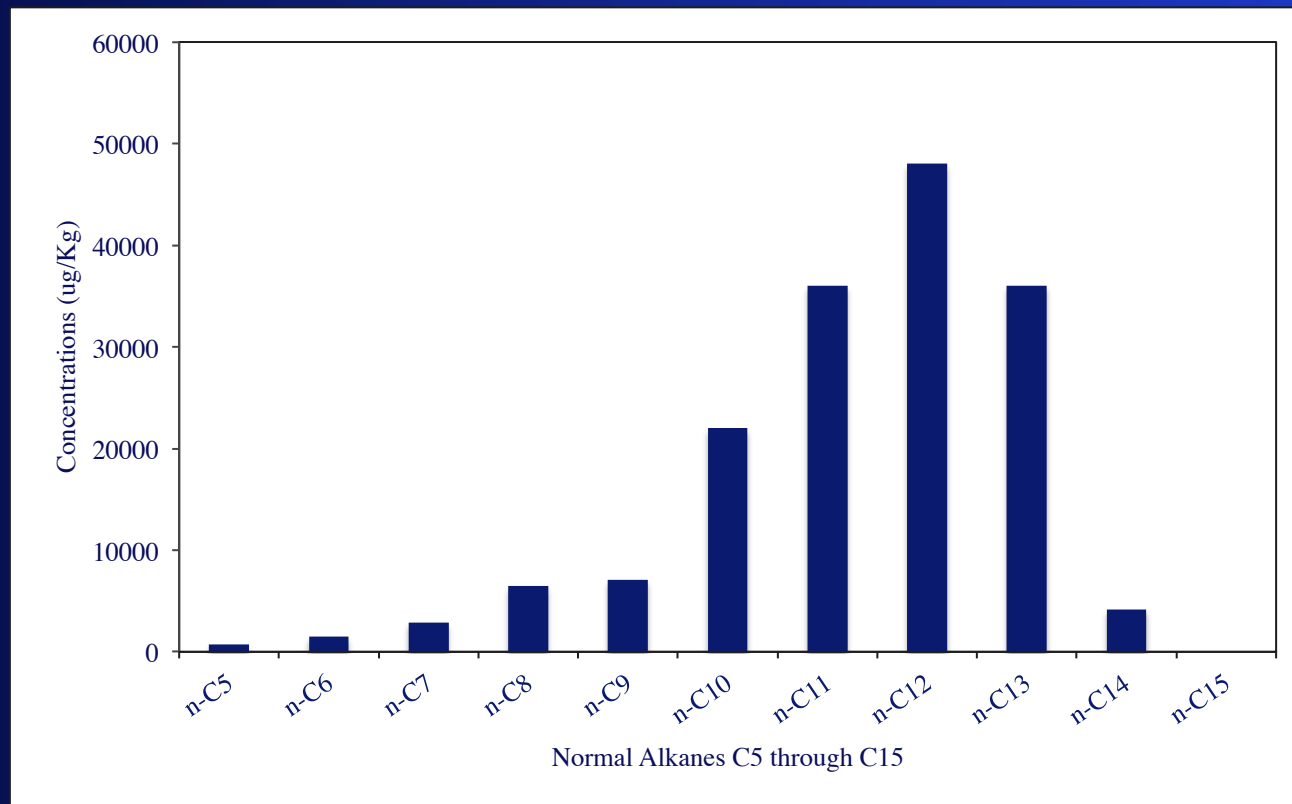
Hydrocarbon degradation statistics

Case 1: UST sludge – leaded gasoline



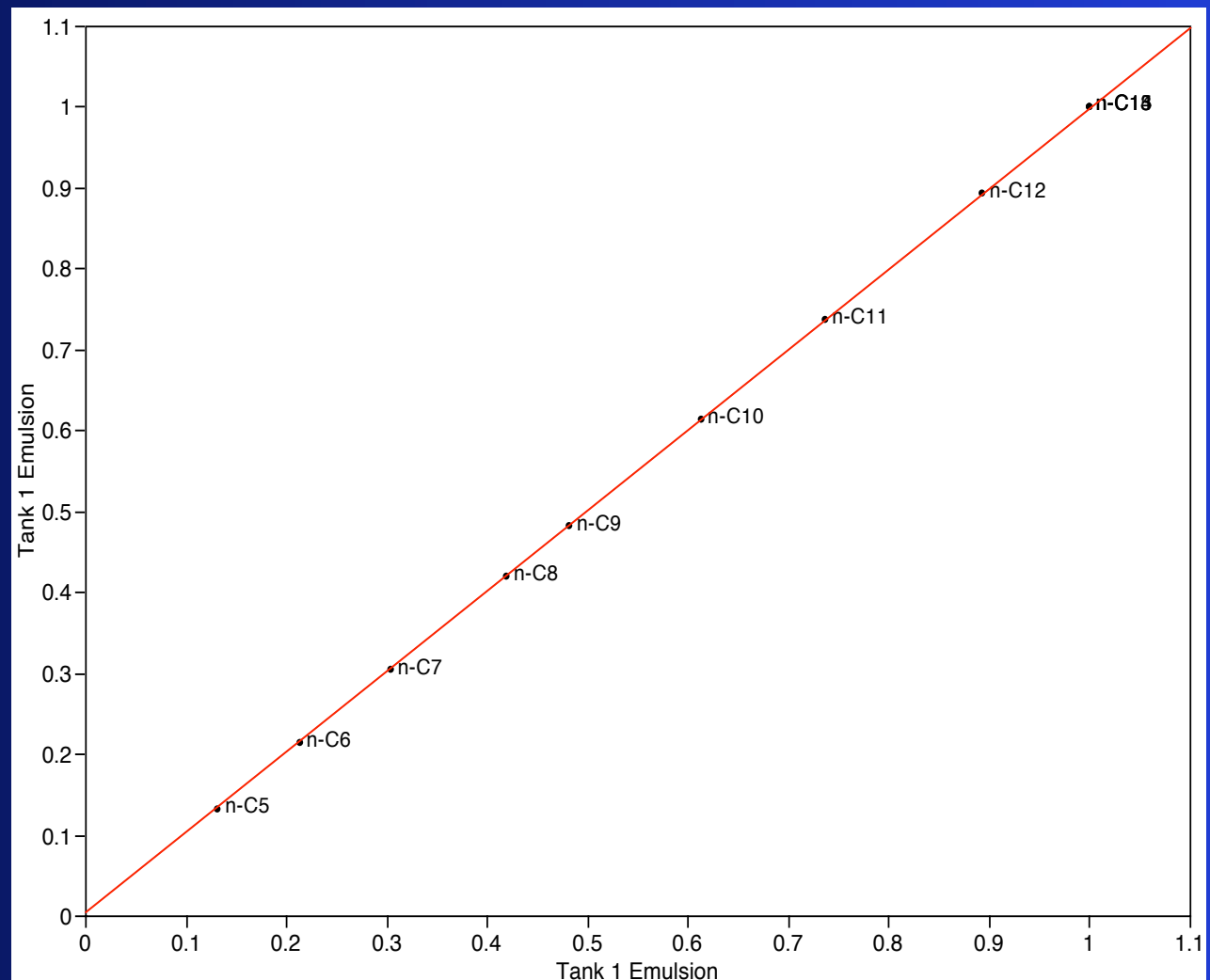
Hydrocarbon degradation statistics

Case 1: soils, down gradient from UST.



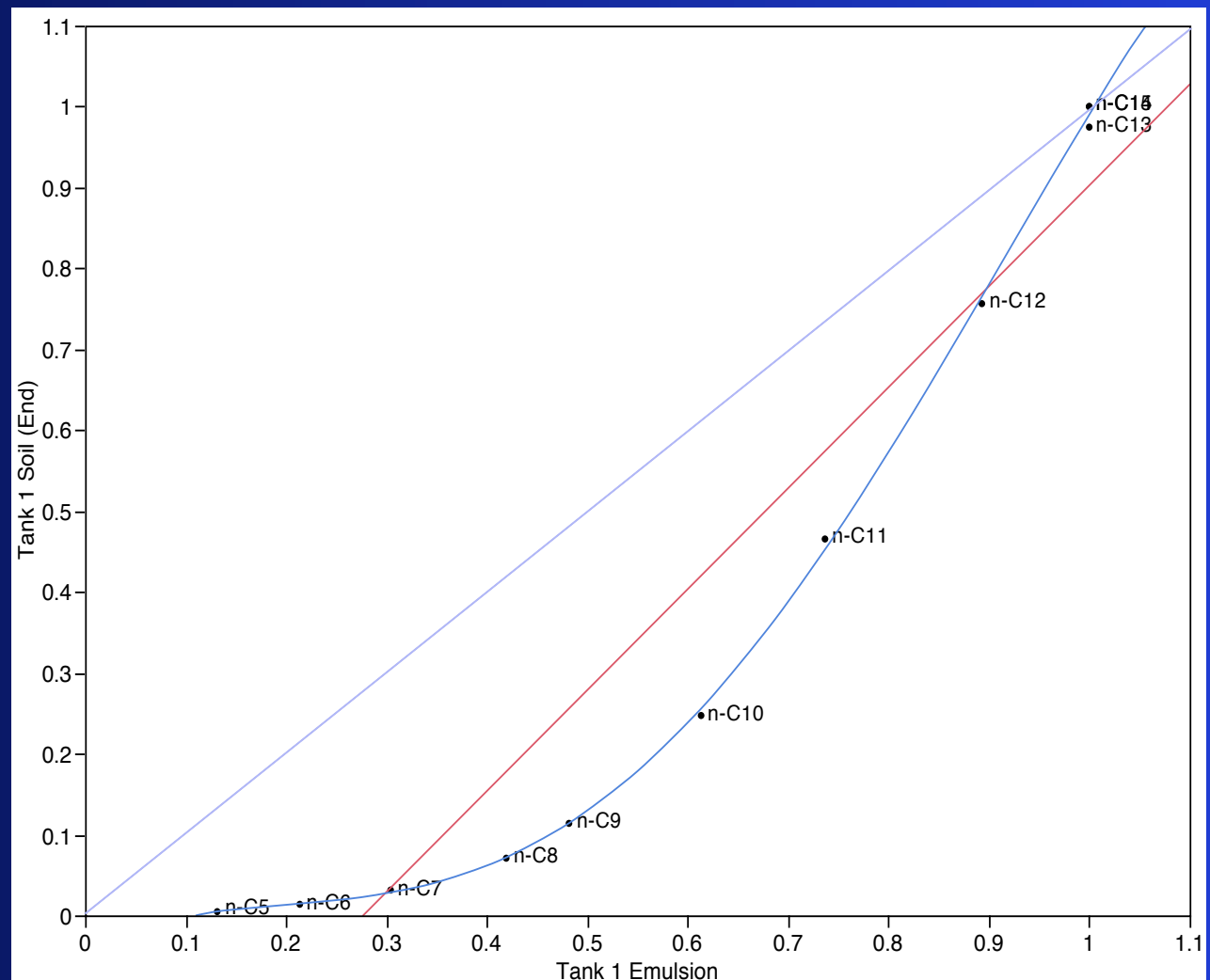
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If we mix one gasoline with only itself, and do a regression for n-alkanes against itself where no HC changes are occurring, we must obtain a straight line.



Hydrocarbon degradation statistics

Case 1: if we compare UST contents (X-axis) with the outside soil HC (Y-axis), a different picture emerges - HC loss, *i.e.*, degradation of n-alkanes.



Hydrocarbon degradation statistics

Case 1 pattern shows loss of n-alkanes in the soil sample compared with the starting material. The curvilinear relationship below the individual alkane line, a mass loss, *i.e.* degradation.

If there were to be a curvilinear relationship above the line, it would mean that individual hydrocarbons have been proportionally added when the UST gasoline was released to the soils. Enrichment does not occur in degradation but may if another HC source is present

Hydrocarbon degradation statistics

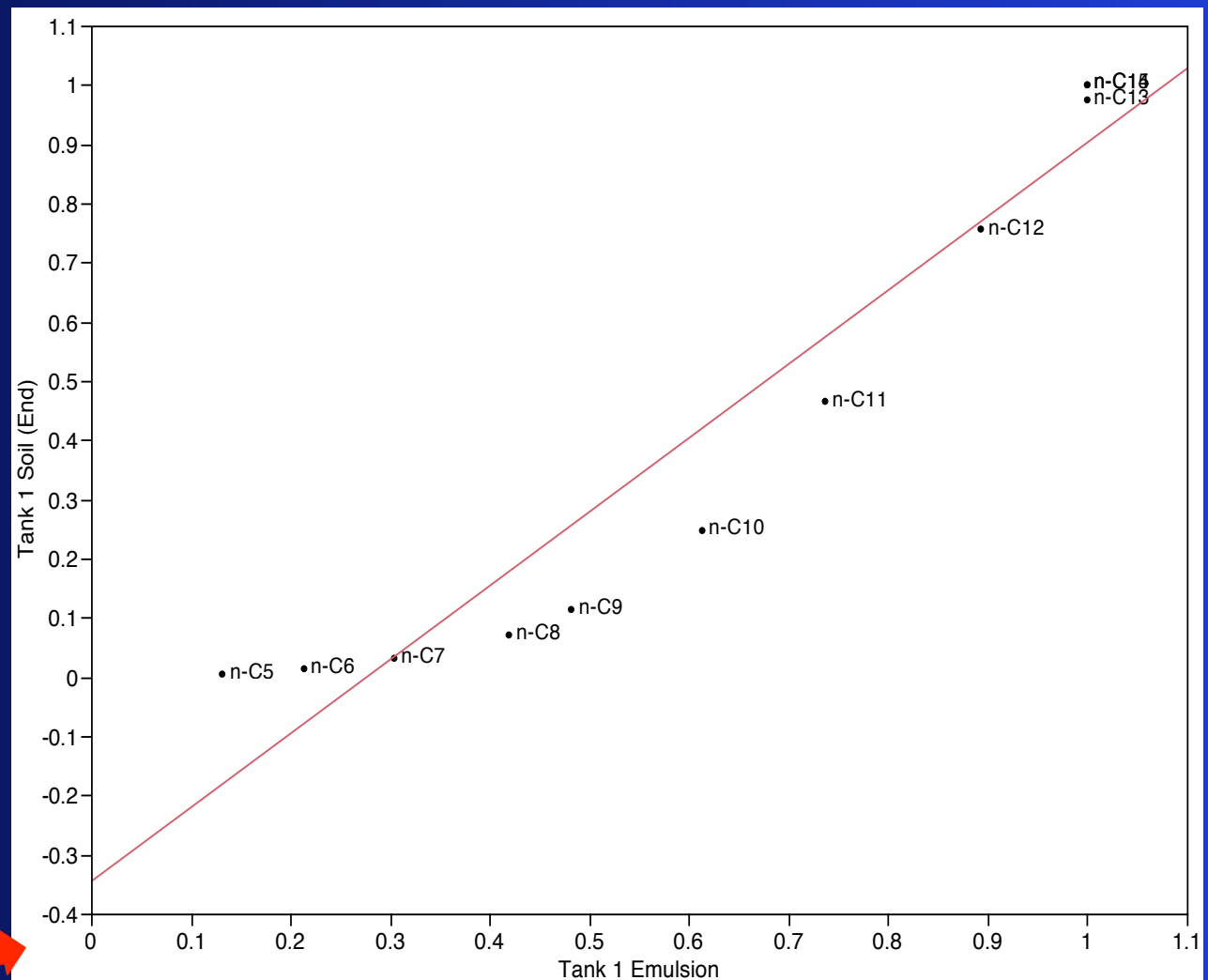
There are two ways of modeling this behavior mathematically for Case 1:

Linear modeling of loss showing how much was lost (or gained) from the Y-axis compared with the starting material.

Polynomial modeling of loss to determine how many factors are needed to define a statistically significant relationship.

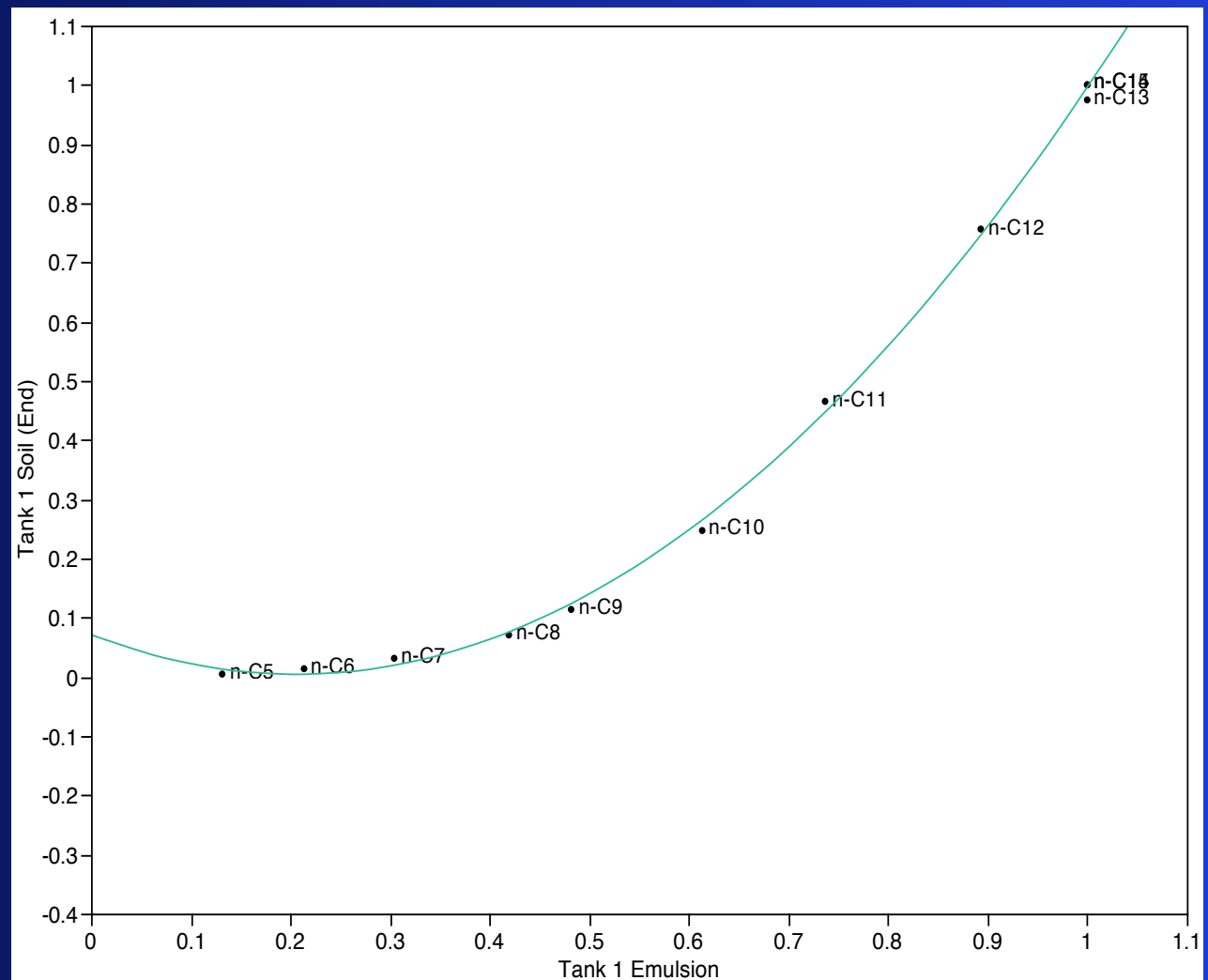
Hydrocarbon degradation statistics

Case 1:
Extending the
Y-axis to the
negative shows
the value of
the b factor in
linear equation
 $Y = mX + b$
Y-axis is
negative



Hydrocarbon degradation statistics

Case 1: But a
($Y = mX + nX^2 + b$) quadratic
model, the two
factors tells us
how many
gasolines we
have, starting
gas and another
(degraded) gas.



Hydrocarbon degradation statistics

This type of analysis can be done for each PIANO fraction in Case 1.

The most important aspect of the analysis is that the linear approach gives us a measure of the % loss of the entire fraction (we have seen only paraffin fraction), while the quadratic approach counts the number of different gasolines we have in the system.

Plus the statistics: r^2 and significance (p values).

Hydrocarbon degradation statistics

What does this analysis give us where one gasoline is not like the other, *i.e.*, not manufactured by the same producer.

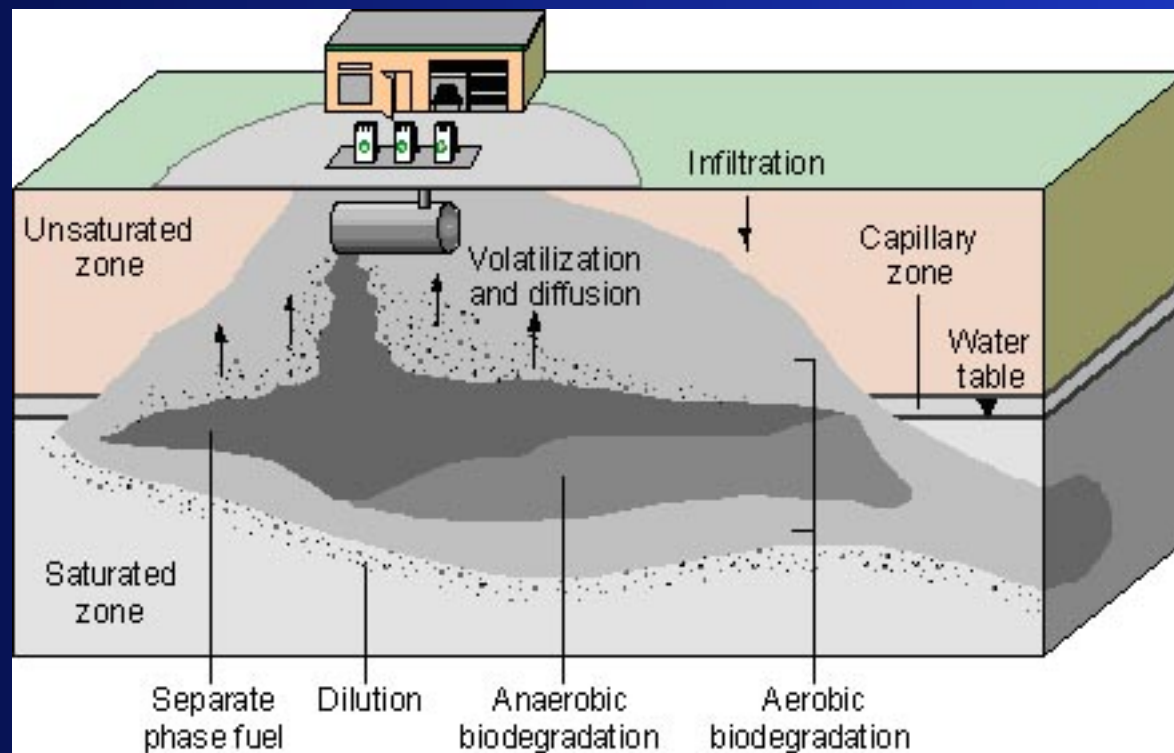
Two alternatives:

Degradation - if solely from 1 source and/or potential mixing from another degraded source.

Enrichment – mixing from 2 or more sources.

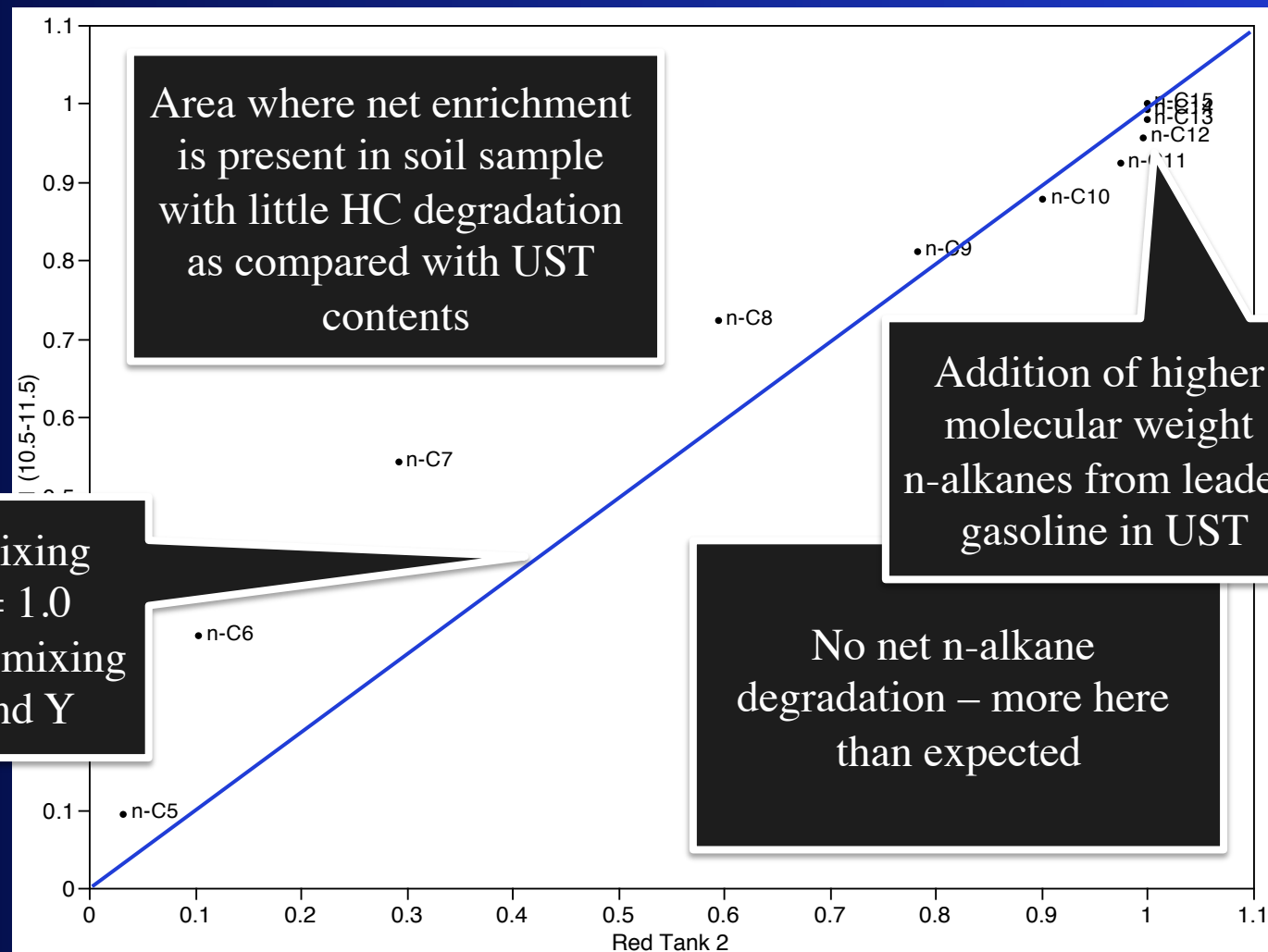
Hydrocarbon degradation statistics

Of course, Case 1 is relatively simple. On the more complex side is Case 2. . .



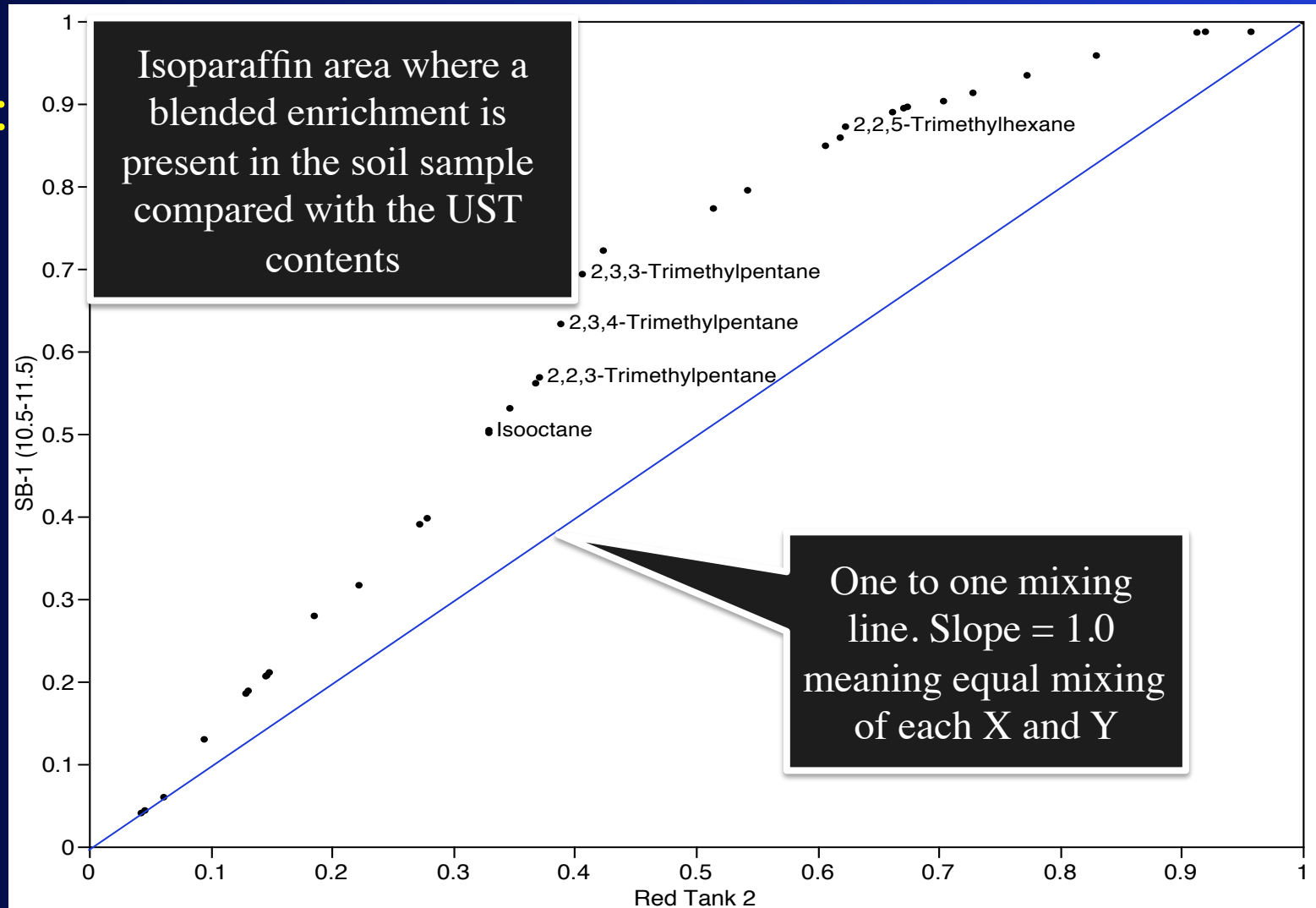
Hydrocarbon degradation statistics

Case 2:



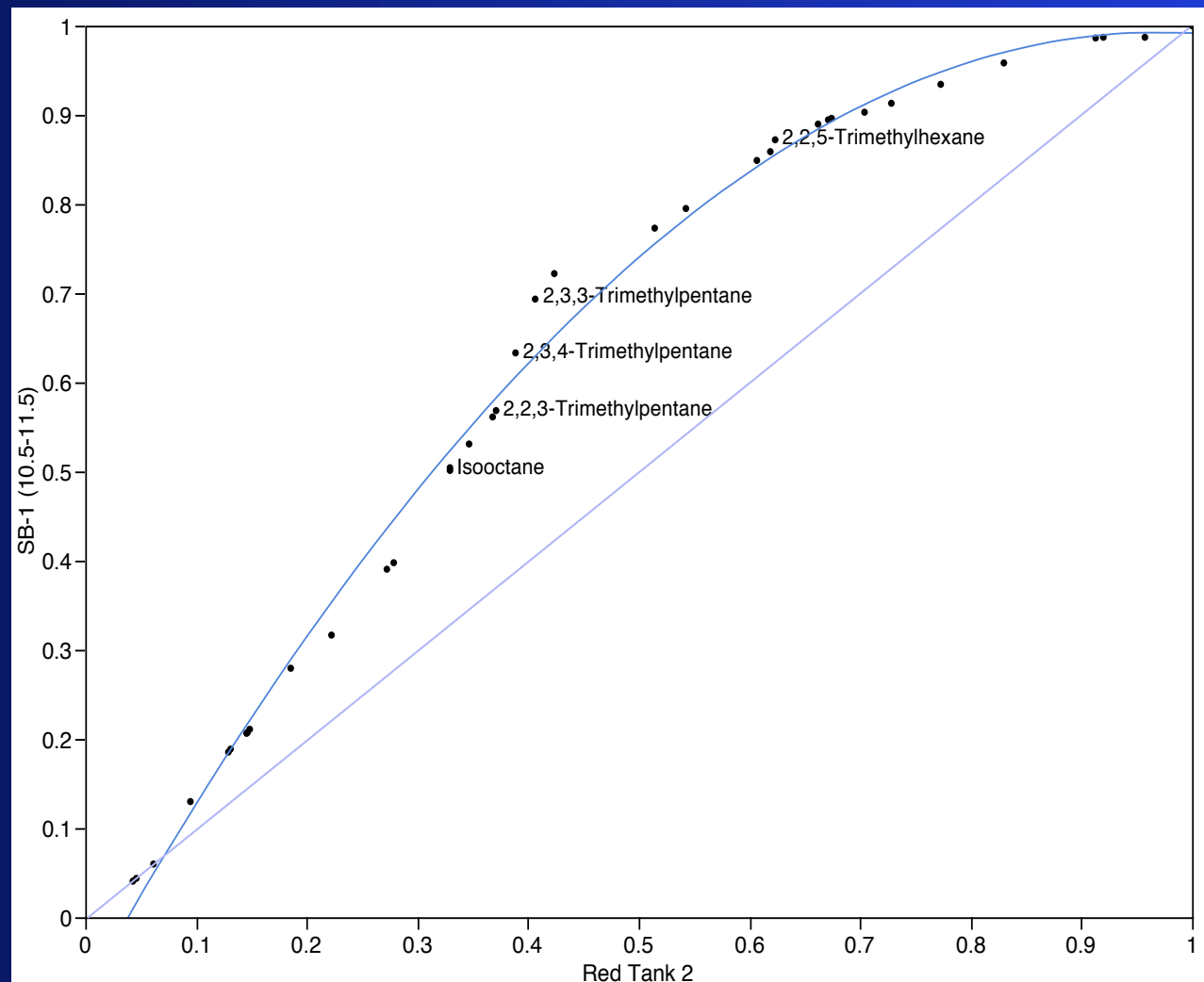
Hydrocarbon degradation statistics

Case 2:



Hydrocarbon degradation statistics

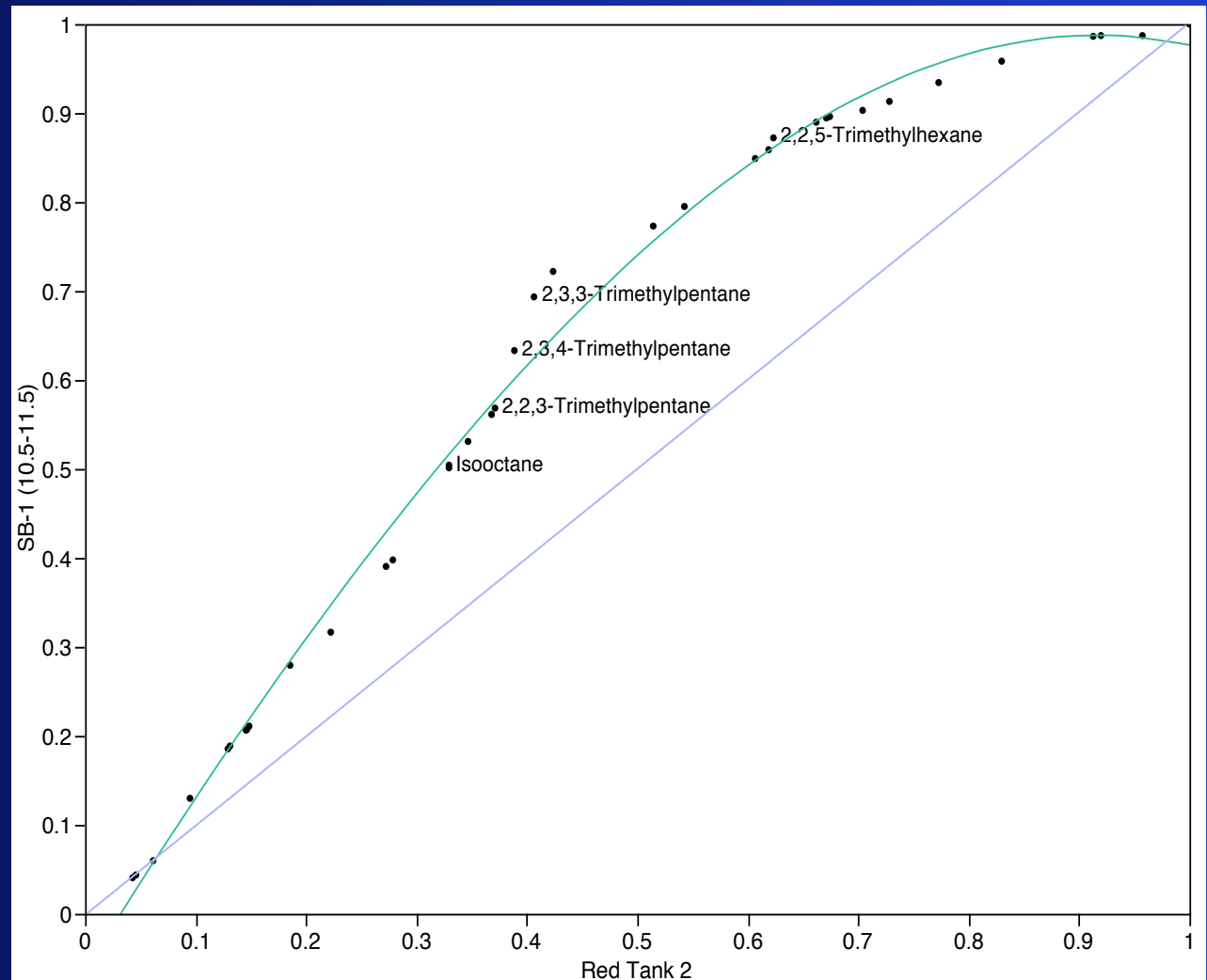
Case 2:
Quadratic,
i.e., 2
factors: a
little more
statistically
significant.



Hydrocarbon degradation statistics

Case 2:
Cubic, i.e.,
3 factors:

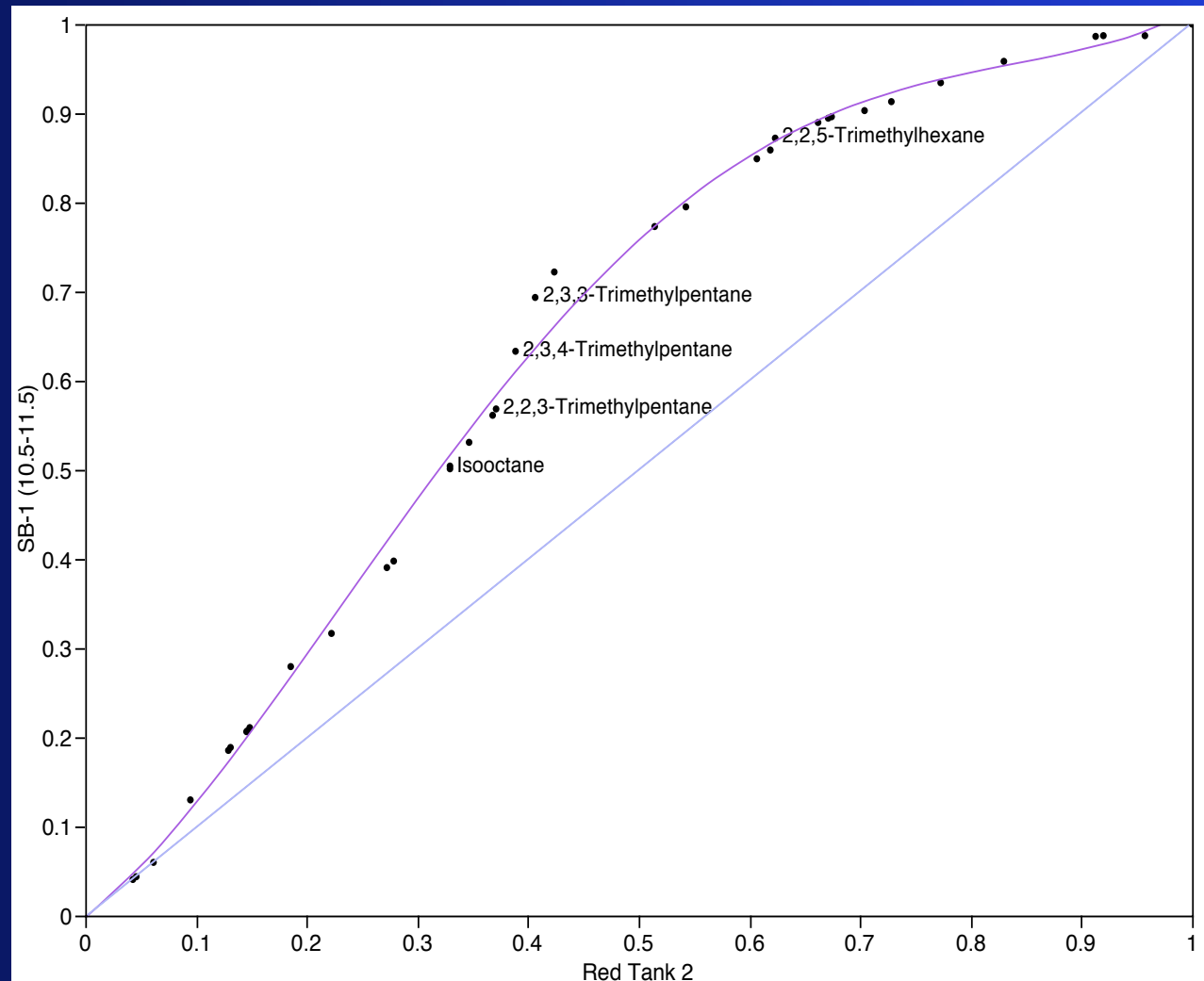
Slightly
more
statistically
significant
yet.



Hydrocarbon degradation statistics

Case 2:
Quartic,
i.e., 4
factors

As the
number of
factors
increases,
 r^2 increases
somewhat.



Hydrocarbon degradation statistics

Again, Case 2 data can be analyzed for each fraction, for each sample for each fraction until all five PIANO fractions have been analyzed.

What the investigator is left with at the end is an understanding of how gasolines in the soils were blended compared with the starting material in the UST being examined for loss.

In Case 2, no loss from the UST, gain once the HCs were in soils, *i.e.*, other sources, not USTs.

Hydrocarbon degradation statistics

The degree of the polynomial defines how many mixing sources there are:

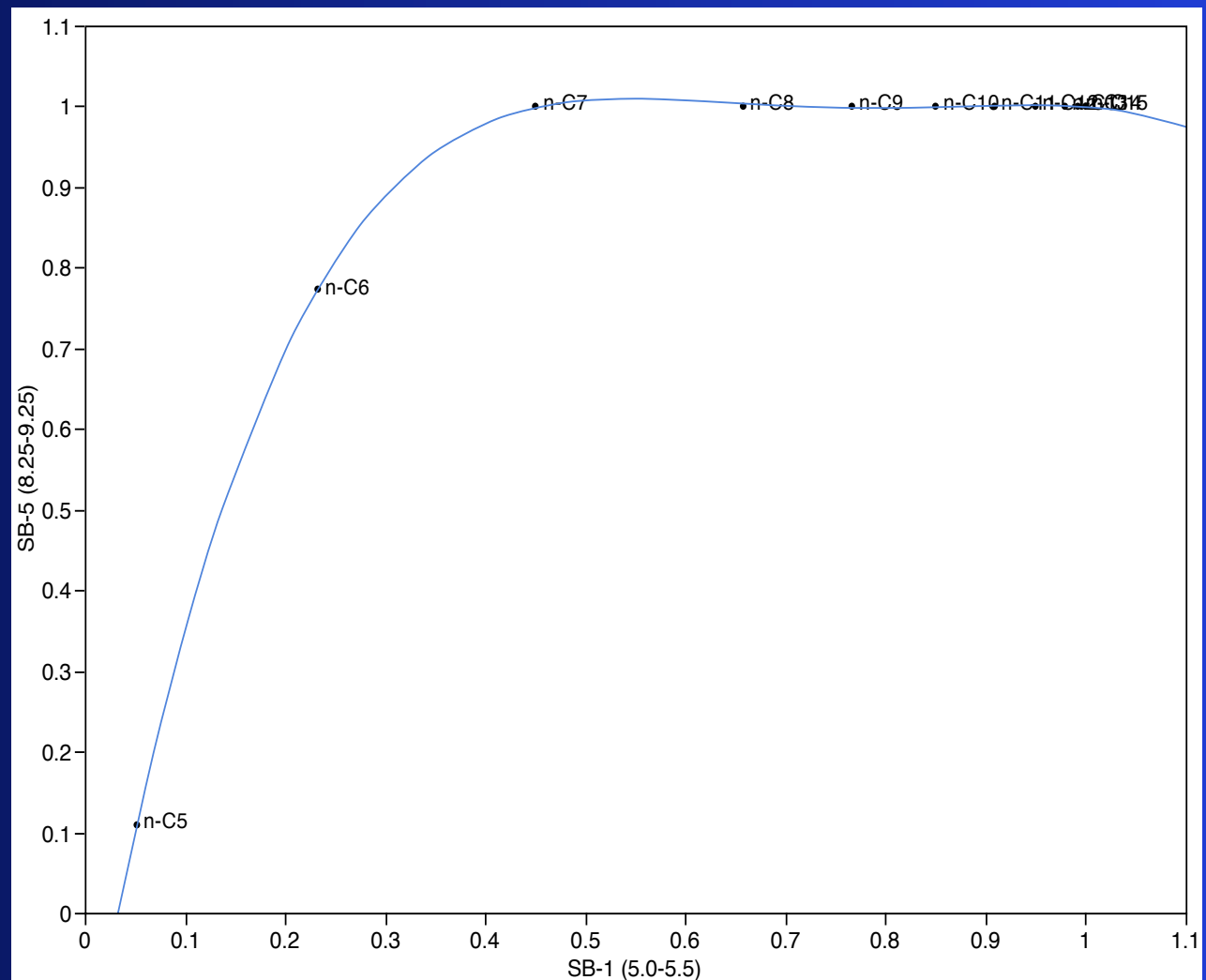
If there is evidence of degradation, then the one in the tank counts as one source to the soil.

If there is no evidence for HC degradation, then the one in the tank does not factor into the count as a source to the soils/sediment because it is not involved in the final composition of the gasoline HC backbone in the soils.

Hydrocarbon degradation statistics

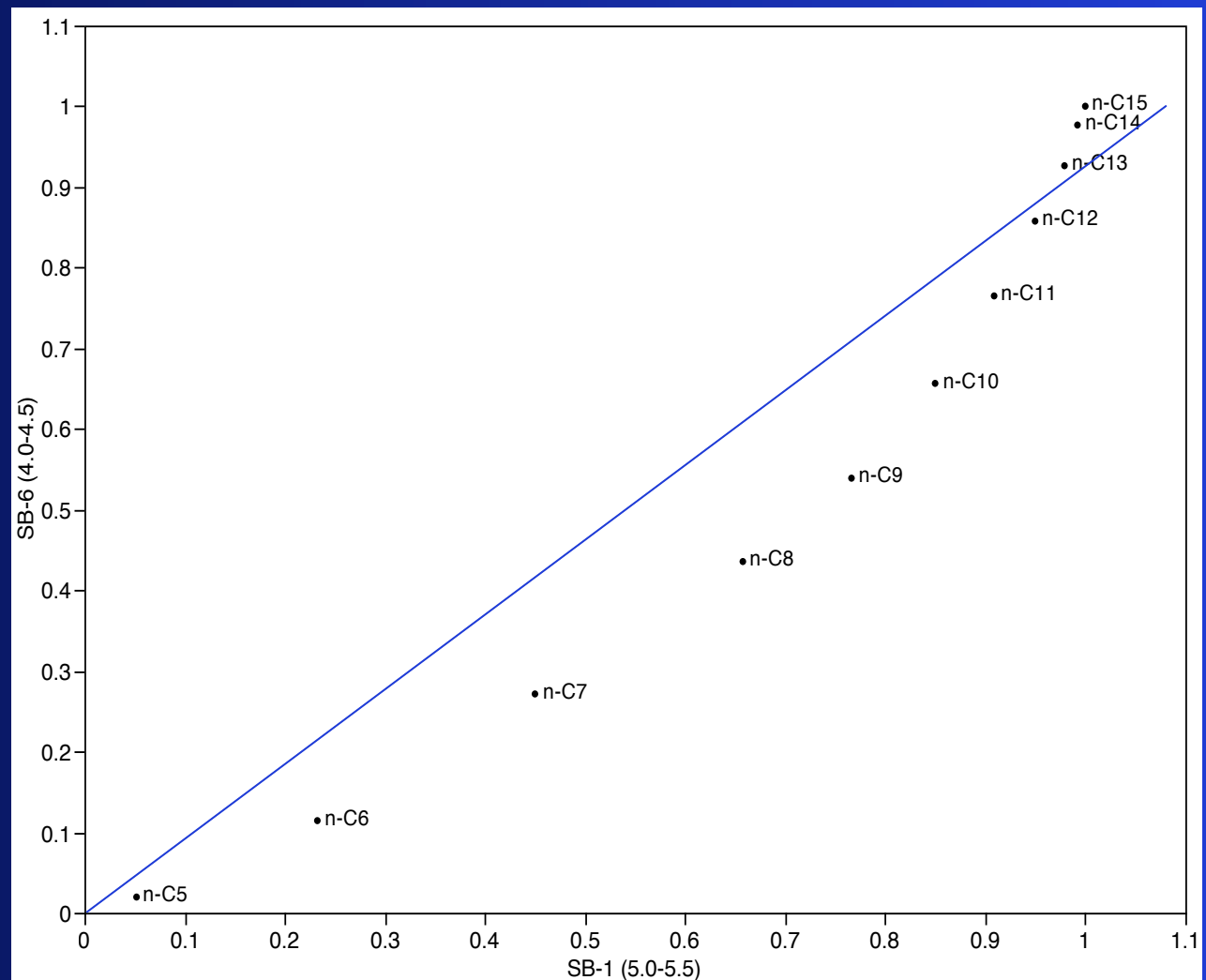
Case 2: What
about soil v.
soil?

SB-5 soils in
Case 2 ...
early
n-alkanes
only v SB-1.



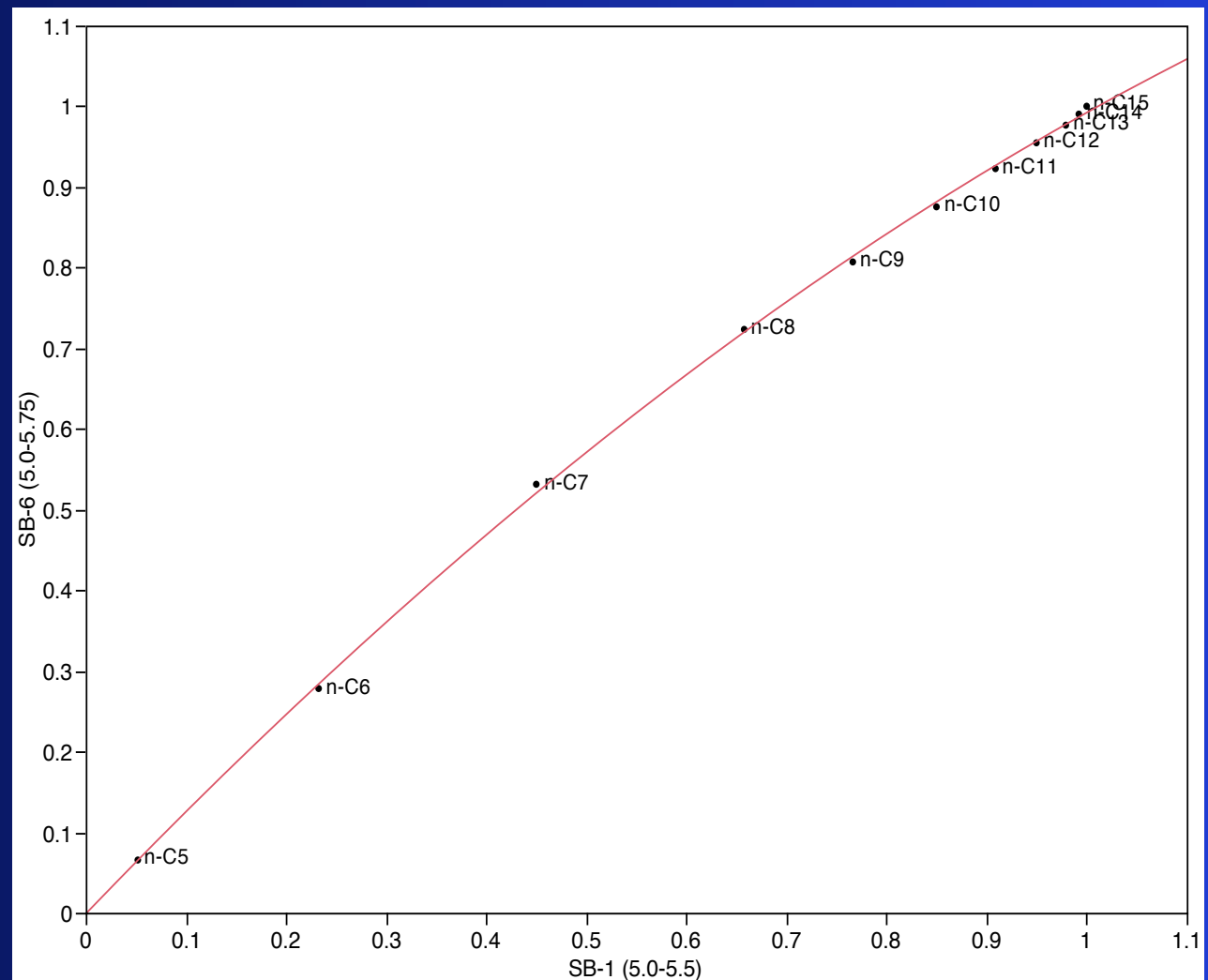
Hydrocarbon degradation statistics

Case 2: SB-5
vs. SB-6
(4-4.5') in
the same type
of analysis,
we find a
different
product mix
in SB-6. Not
from USTs
but related.



Hydrocarbon degradation statistics

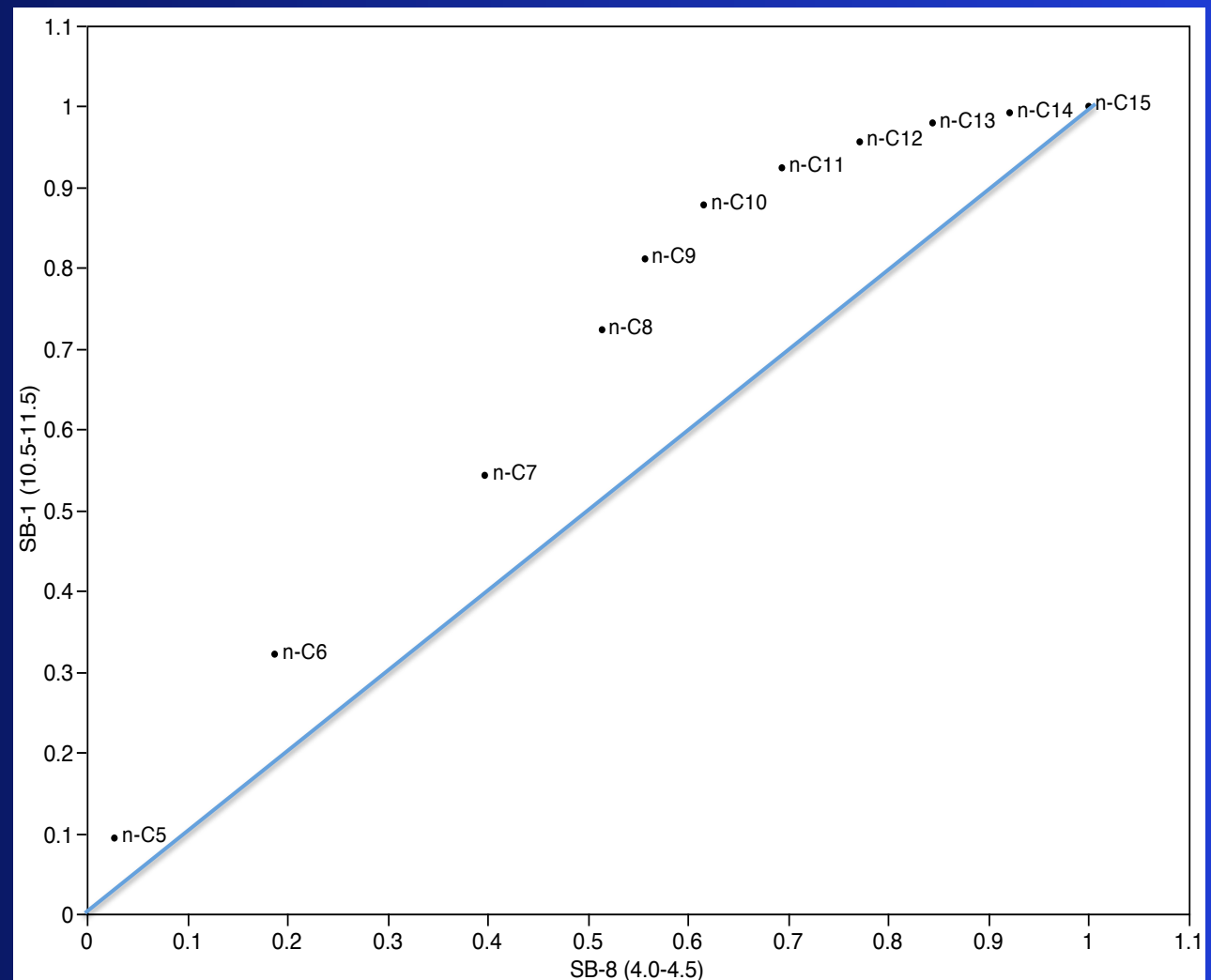
Case 2: SB-6 (5-5.5)' in the same location has a different product mix deeper into SB-6 than at shallower depths.



Hydrocarbon degradation statistics

Case 2: the comparison of SB-1 (10.5-11.5') with SB-8.

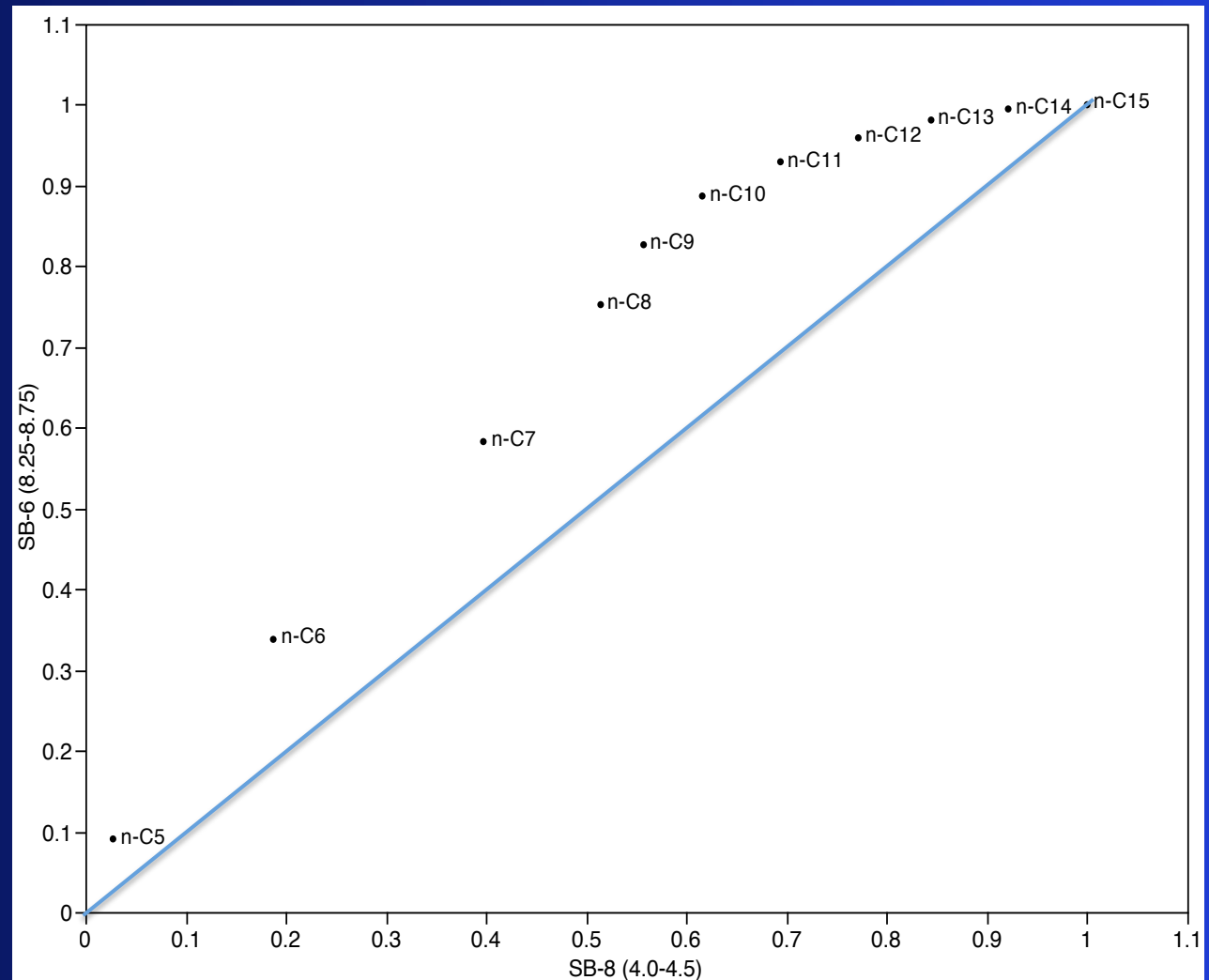
Evidence of two product distributions.



Hydrocarbon degradation statistics

Case 2: SB-6
(8.25-8.75')
with SB-8.

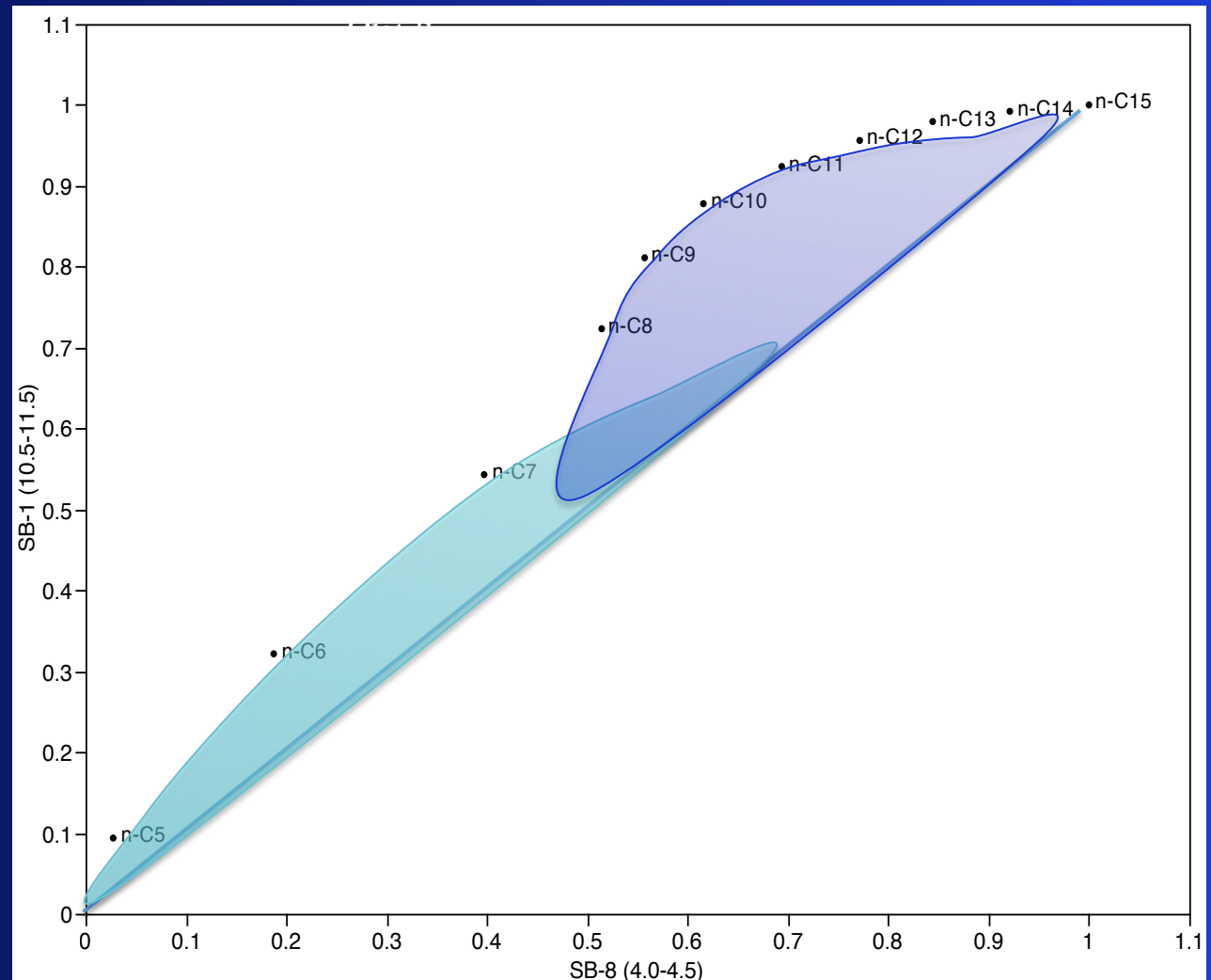
Evidence of
two different
distributions.



Hydrocarbon degradation statistics

Case 2: Can we measure under the curves? Yes, of course.

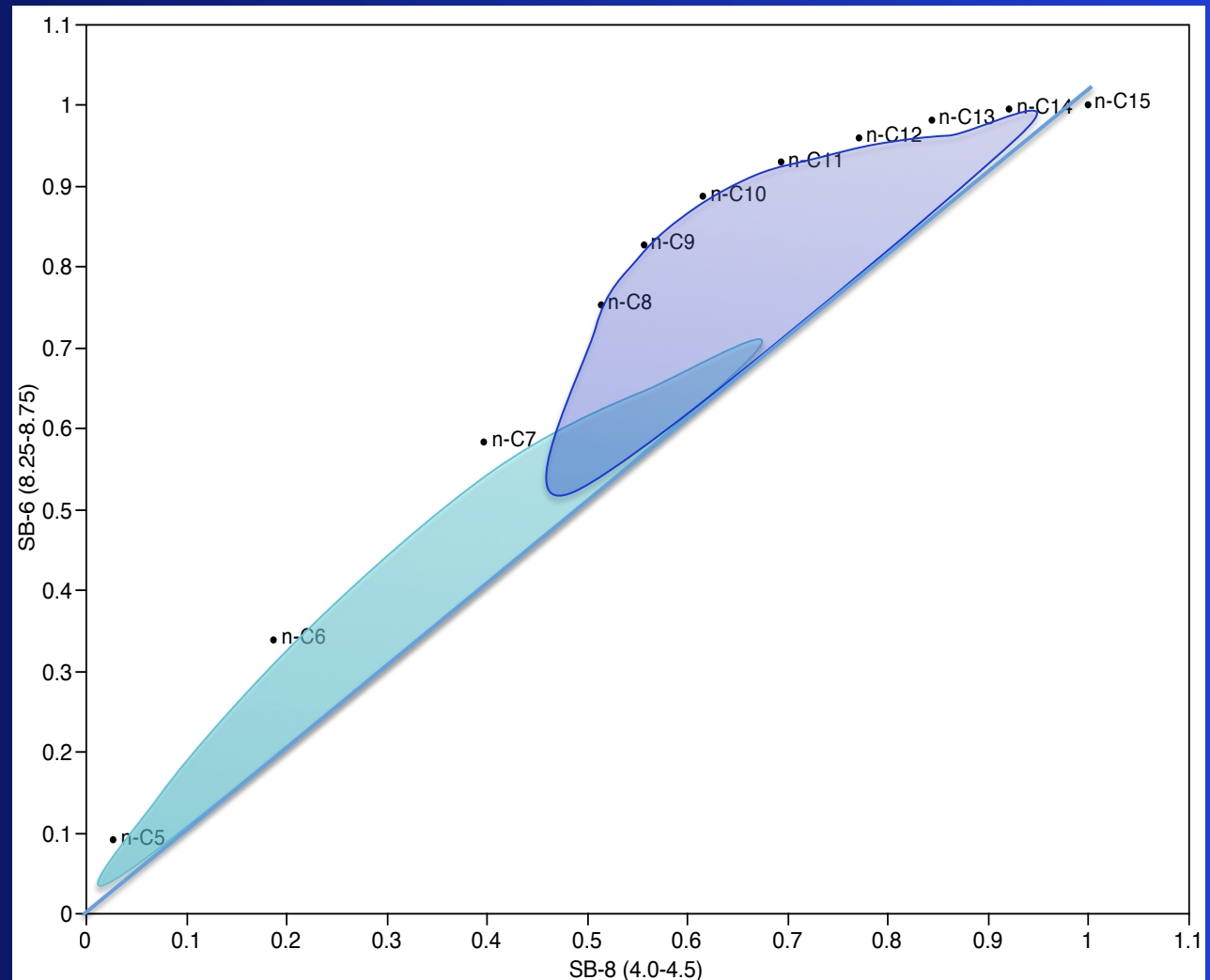
Data show 45:55 and 10% overlap between products.



Hydrocarbon degradation statistics

Case 2: For shallower depth at SB-6, the approach, appears to be similar . . .

. . . and data 45:56 and 9 % overlap, *i.e.* virtually identical.



Hydrocarbon degradation statistics

Best of all, the principles remain the same regardless of scenario. Degradation or enrichment for any UST content model can be used to examine hypothesis testing of UST release(s) for a variety of products.

Case 1 & 2 hydrological analyses demonstrated that release of petroleum products from different tanks would have impacted same loci. Chemical data, thus, reinforced the hydrological transport models for each site.

Hydrocarbon degradation statistics

Both chemical and geological/hydrological results were consistent with the types and timing of petroleum product sales as determined by depositions and/or attorney records search completed for both cases.

On site photography played critical role.

Overall synthesis approach has been written about and discussed in international technical conferences and applied in litigation.

Hydrocarbon degradation statistics

Conclusion:

Pattern assemblage is the focusing of statistics and geochemical principles which produces simple, easily understood “jury exhibits.”

Allows an investigator to explain complicated science to non-scientific audiences in a simple manner.

Scientific Question: Why collect an array of geochemical data if you are not going to use it?

Hydrocarbon degradation statistics

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