Forensic Characterization of Gasoline Releases Impacting the Environment

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What is forensics?

My definition:

1. The use of expertise to resolve disputes[1, 2].

And environmental forensics?

- The use of environmental expertise to resolve disputes, or
- The use of expertise to resolve environmental disputes.

[1] Oudijk, G. 2005. Fingerprinting and age dating of gasoline releases - A case study. *Environmental Forensics* 6 (3): 2-10.
[2] There are many different definitions of "environmental forensics". I am providing just one of many.

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Why Is This Important?

The USA manufactures about 300,000,000 gallons (1,200,000,000 litres) of gasoline per day. Canada, Europe & Japan, etc. are not far behind per capita.

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So?

Even if the spillage rate is 0.01%, the amount of gasoline released would still be more than 30,000 gallons (>100,000 litres) per day, just for the USA. Let's hope we're doing better than 0.01%!

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And Why Is This A Problem?

No one wants to pay for the cleanups. They're expensive!

This Is Where I Come In

Might there be other responsible parties to help pay for these cleanups? The forensic techniques described here can be helpful if there are.

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How Do We Determine This?

- *Fingerprinting*: What type of gasoline is it? Regular? Premium? How was it manufactured? Who manufactured the gasoline? (This one is often very difficult: gasoline is fungible).
- *Age dating*: When was the gasoline manufactured? How old is the release?
- This information often allows us to determine who was responsible for the release.

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PIANO

A PIANO analysis is a laboratory procedure through gas chromatography coupled with mass spectroscopy. PIANO is an acronym for *n*-Paraffins (P), *Iso*-paraffins (I), Aromatics (A), Naphthenes (N) and Olefins (O), what this analysis can detect. Oxygenates can also be identified through this analysis.

Many or most of our fingerprinting and age-dating questions can be answered through a PIANO analysis.

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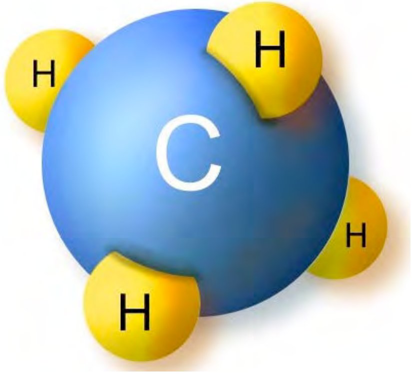
What Does a PIANO Analysis Give Us?

Identification and quantification of 500 to 1,000 different hydrocarbons in the gasoline and presented in either weight%, volume% or molar concentration.

IMPORTANT! Many of these hydrocarbons would not be identified on the normal scans used for regulatory compliance.



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First, organic chemistry, ugh..

Paraffins (P) or “normal alkanes”: straight-chain saturated (“aliphatic”) hydrocarbons (C_nH_{2n+2});
Iso-Paraffins (I) or “*iso*-alkanes”: branched-chain saturated hydrocarbons (C_nH_{2n+2});
Aromatics (A): carbon chains with a double bound after every second carbon (C_nH_{2n-6});
Naphthenes (N) or “*cyclo*-alkanes”: saturated carbon chains (C_nH_{2n+2});
Olefins (O) or “alkenes”: unsaturated hydrocarbons with double bounds (C_nH_{2n}).

These are the predominant hydrocarbons in gasoline (plus the oxygenates).

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What Does the Laboratory Need for a PIANO Analysis?

- Separate-phase gasoline: More than a sheen, at least a film of gasoline, preferably a layer.
- Soil? The analysis can be performed, but because of hydrocarbon adsorption, it might impact our interpretation of the results (you will see why soon).

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Who Can Perform a PIANO Analysis?

PIANO analyses are normally performed for the oil industry. But there are many labs now in the environmental field that perform this analysis. (Maxxam Analytics in Edmonton probably does the best one and includes the most hydrocarbons)[1, 2].

[1] An honest disclosure: Maxxam is a client of ours.

[2] Maxxam's PIANO analysis provides data on about 1,000 hydrocarbons

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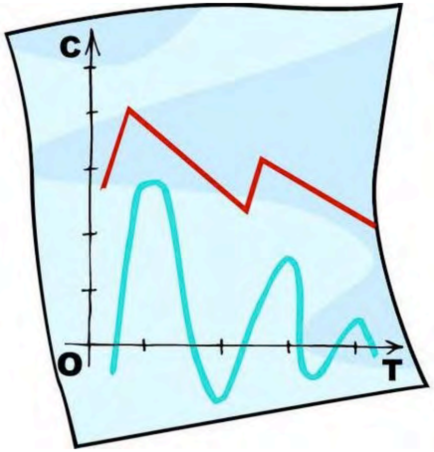
Our Interpretation

We look at three factors:

- the magnitude of environmental weathering;
- refining characteristics: the types of methods used, the grade of gasoline, etc., and
- compliance with regulatory requirements (in the USA: known as "reformulated gasoline").

This information will help us to characterize the gasoline.



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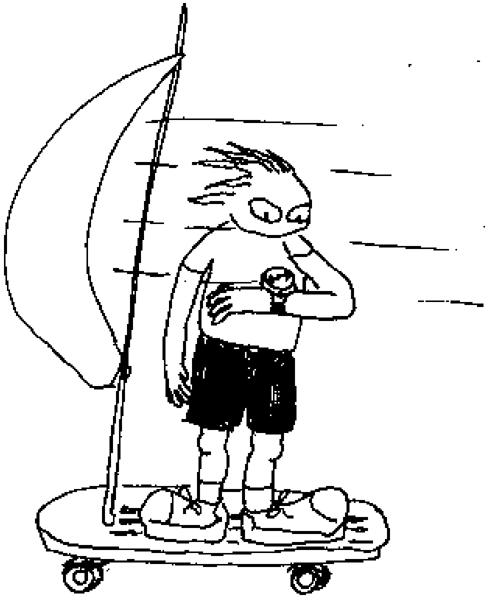
The "Diagnostic Ratios"

We look at several ratios of the hydrocarbons obtained from the PIANO scan. Normally, they are hydrocarbons of the same molecular weight, but with different environmental characteristics, such as volatility, solubility or biodegradability.



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These diagnostic ratios come from:

Peters, K. E., Walters, C. C. & Moldowan, J. M. 2007. *The Biomarker Guide: Volume 1, Biomarkers and Isotopes in the Environment and Human History*, 2nd Edition. Cambridge, UK: Cambridge University Press.

Kaplan, I. R., Galperin, Y., Lu, S-T. & Lee, R-P. 1997. Forensic environmental geochemistry: Differentiation of fuel types, their sources and release time. *Organic Geochemistry* 27:289-317.

These two publications are important references in hydrocarbon forensics.

If you want to do age dating or fingerprinting of gasoline releases, get your hands on these publications (plus mine, of course ☺).

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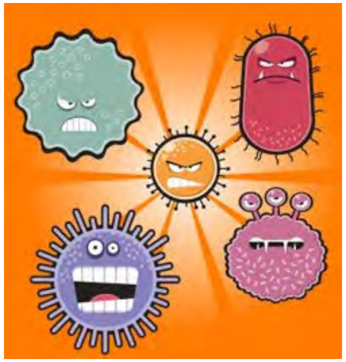
Biodegradation Ratios

(*iso*-paraffins+naphthenes)/*n*-paraffins

Gives us an approximation of the magnitude of biological alteration ("biodegradation"). Normally ranges from about 2 to 10 in fresh gasoline. The ratio increases as biodegradation proceeds because the *iso*-paraffins and naphthenes (*cyclo*-alkanes) are more resistant to biological alteration compared to the *n*-paraffins.



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Biodegradation Ratios (Cont'd)

Methyl-*cyclo*-hexane/*n*-C_7 (n-heptane)

Normally, around 0.5 to 2.0 in fresh gasoline, but can vary. The ratio increases as biodegradation proceeds because methyl-*cyclo*-hexane is more resistant to biological alteration compared to *n*-heptane.

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Dissolution Ratios

[Benzene + Toluene]/[Ethylbenzene + *o,m,p*-xylenes][1]

In fresh gasoline, the ratio normally ranges from about 0.8 to 1.1. The ratio declines as dissolution of the aromatics proceeds because benzene and toluene are more water soluble compared to ethylbenzene and the *o,m,p*-xylenes. However, highly dependent on the geochemical conditions. Under anaerobic conditions, the ratio could reverse! So be careful!

[1] There's an article out there that says that this ratio is total hogwash. So read it and be careful!

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Dissolution Ratios (Cont'd)

Benzene/*cyclo*-hexane

Provides an approximation of the magnitude of dissolution or "water washing". The ratio is normally, between 0.5 and 2.0 in fresh gasoline. The ratio declines as dissolution proceeds because benzene is more water soluble compared to *cyclo*-hexane.

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Dissolution Ratios (Cont'd)

Toluene/methyl-*cyclo*-hexane

Normally, the ratio ranges from about 2 to 10 in fresh gasoline. The ratio declines as dissolution proceeds because toluene is more water soluble compared to methyl-*cyclo*-hexane.

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The Evaporation Ratios
n-pentane (*n*-C_5)/*n*-heptane (*n*-C_7)

The ratio provides an approximation of the magnitude of evaporation. Normally, the ratio is around 0.5 to 2 in fresh gasoline. The ratio declines as evaporation proceeds because *n*-pentane is more volatile compared to *n*-heptane.

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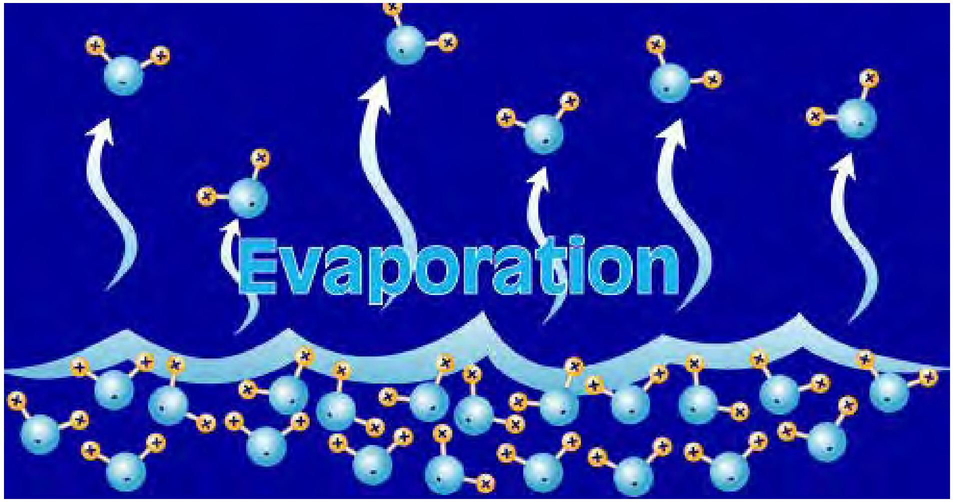
Evaporation Ratios (Cont'd)

2-methylpentane/2-methylheptane

Normally, the ratio is between about 3 and 8 in fresh gasoline. The ratio declines as evaporation proceeds because 2-methylpentane is more volatile compared to 2-methylheptane.



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Evaporation ratios: the type of release

With the evaporation ratios, we can often assess whether the release was aboveground or underground; for example, from (1) an underground tank or subsurface pipeline or (2) an aboveground tank. Gasoline from releases that had any residence time in contact with the atmosphere will normally be more evaporated.

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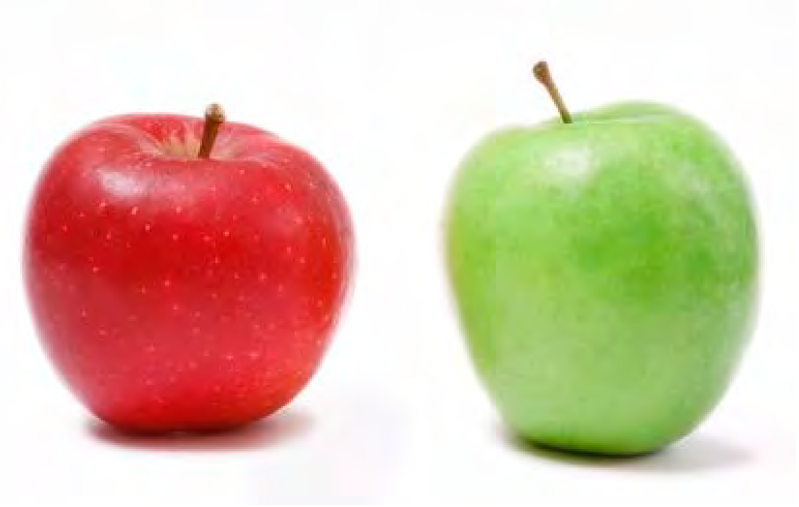
Compared to what?

You should compare your PIANO results to a PIANO analysis of a local and recent gasoline. Don't compare your results from Rotterdam (sea level) to 1980 gasoline from Switzerland (in the mountains).



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Example from Connecticut 2010

Method	Formula	NAPL sample MW-8	*Comparison:* 2008 Exxon regular unleaded gasoline[1]	2008 Gulf regular unleaded gasoline[1]	Significance	Explanation
Environmental:						
Biodeg	(*iso*-paraffins+naphthenes)/*n*-paraffins	4.61	2.29	8.54	Biodegradation minimal	Ratio increases as biodegradation proceeds because the *iso*-paraffins and naphthenes are more resistant to biological alteration compared to the *n*-paraffins.
Biodeg	MCH/*n*-C_7	0.70	0.57	0.84	Biodegradation minimal	Ratio increases as biodegradation proceeds because methyl-*cyclo*-hexane is more resistant to biological alteration compared to *n*-heptane.
R_b	(B+T)/(E+X)	0.04	1.12	1.07	Dissolution significant	The ratio declines as dissolution of the aromatics proceeds because benzene and toluene are more water soluble compared to ethylbenzene and the *o,m,p*-xylenes.
Water wash	B/*cyclo*-hexane	0.00	0.45	1.41	Dissolution significant	The ratio declines as dissolution proceeds because benzene is more water soluble compared to *cyclo*-hexane.
Water wash	toluene/MCH	0.22	9.25	5.6	Dissolution significant	The ratio declines as dissolution proceeds because toluene is more water soluble compared to methyl-*cyclo*-hexane.
Evap	*n*-pentane/*n*-heptane	0.00	0.13	0.23	Evaporation significant	The ratio declines as evaporation proceeds because *n*-pentane is more volatile compared to *n*-heptane.
Evap	2-methylpentane/2-methylheptane	0.62	7.49	4.83	Evaporation significant	The ratio declines as evaporation proceeds because 2-methylpentane is more volatile compared to 2-methylheptane.

Comparing 1980s gasoline from Waterbury, CT to known examples of 2000s gasoline from New Jersey service stations. NOTE: No refineries in New England since World War II. Has gasoline changed since the 1980s? Yes, very much.

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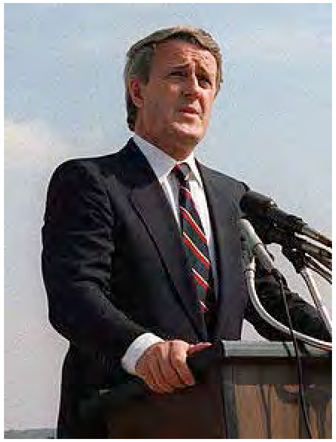
How has gasoline changed since the 1980s?



***Regulatory changes*:**
•No lead (since 1990)
***Reformulated gasoline (since 1998 (Canada), 1996 (Europe) and 1995 (USA)*:**
•Less benzene;
•Less olefins;
•More oxygenates, and
•Lower vapor pressure.
***Meeting octane requirements*:**
•More toluene;
•More oxygenates,
•Less normal alkanes.

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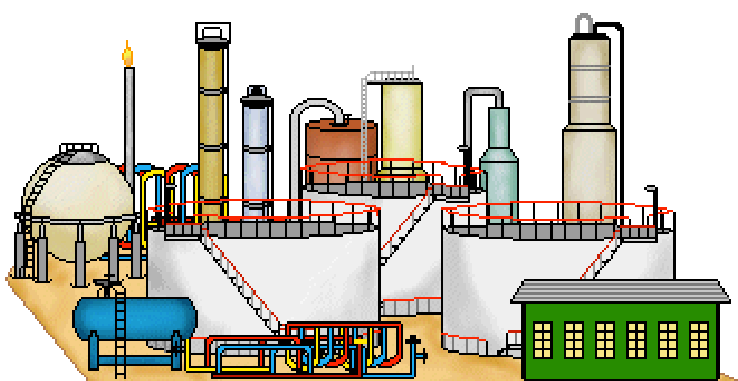
Refining Ratios

2,2,4-trimethylpentane (*iso*-octane)/methyl-*cyclo*-hexane

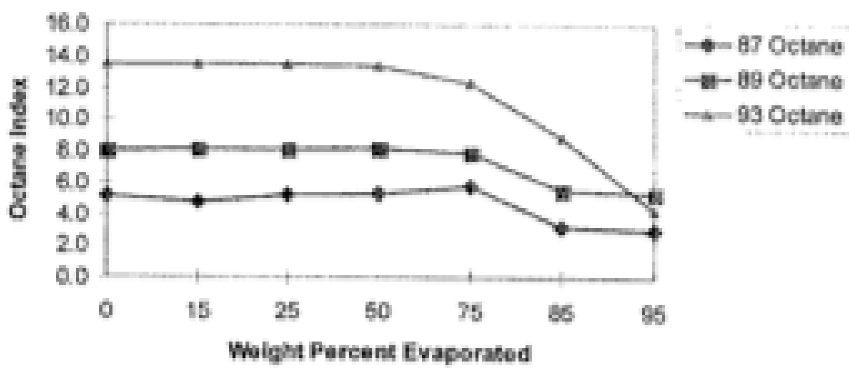
Values greater than 5 normally represent a premium grade (such as 92 octane). Less than 5 are regular grade. 2,2,4-trimethylpentane is the same as iso-octane (*i*-C_8), which is the basis of the octane rating index. Gasoline with 100 % *i*-C_8 would have an octane rating of 100.



Refining Ratios

Octane index (OI) = (2,2,4-trimethylpentane+toluene)/(n-C_7+n-C_8)

Value increases with octane rating; however, toluene, n-C_7 and n-C_8 are susceptible to environmental weathering. As the gasoline becomes more evaporated, it becomes more difficult as shown below.



Source: Schmidt et al., 2003)

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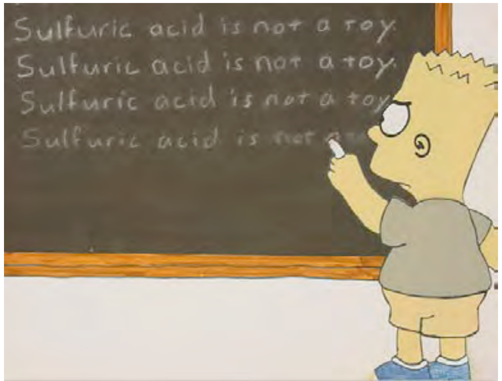
Refining Ratios (Cont'd)

2,2,4-tmp/(2,2,4-tmp+2,2,3-tmp+2,3,4-tmp+2,3,3-tmp)

Alkylation is the transfer of an alkyl group from one molecule to another. The most important alkylation process is the reaction with a catalyst (normally sulfuric or hydrofluoric acid) of *iso*-butane with olefins to produce *iso*-octane. Values between 0.54 and 0.73 represent hydrofluoric acid (HF) alkylation, whereas values between 0.39 and 0.45 represent sulfuric acid (H_2SO_4) alkylation. Alkylation is a refining technique used to produce high-octane *iso*-alkanes, like i-C_8.



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Refining Ratios (Cont'd)

$n\text{-}C_4/(n\text{-}C_4 + iso\text{-}C_4)$

Iso-butane is often removed in modern gasolines to be used as a feedstock in chemical manufacturing; however, both butanes are susceptible to volatilization in the subsurface.

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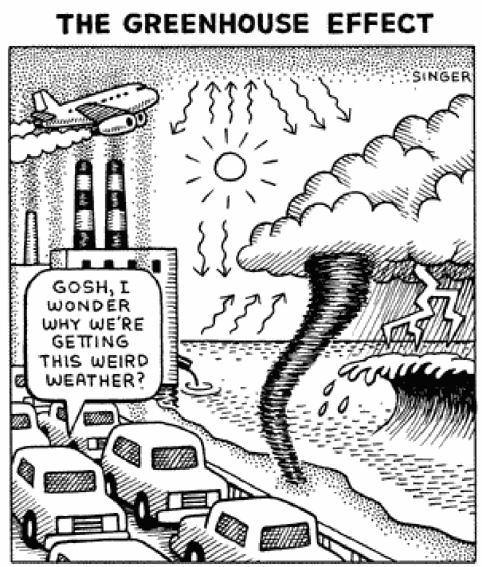
Refining Ratios (Cont'd)

$iso\text{-}C_5/(iso\text{-}C_5+n\text{-}C_5)$

Isomerization is the conversion of straight-chain molecules to higher-octane branched molecules for blending into gasoline or as a feed into alkylation units. It normally imparts on the gasoline a pentane ratio >0.70.



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Refining Ratios (Cont'd)

naphthalene/nC_{12}

Ratio is normally 1 to 3 in fresh gasoline. Reforming is a refining process used to produce aromatics. Higher values indicate that high concentrations of aromatics are or were in the gasoline.

" You smell like mothballs. "

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Conventional versus reformulated parameters

		US	Canada
Benzene	< 1%	1995	1998
Oxygenates	>2%	1995	1998
Total aromatics	<35%*	1995	1998

These parameters are for North America. There are similar regulations in Europe.

* Not a regulation, but vapor-pressure limit normally cannot be met with total aromatics at >35%.

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European changes to gasoline composition in 1996

	Europe	USA	California	Canada
When?	1996	1995	1994	1998
Benzene (vol%)	5	1	2	1
Oxygen	na	>2	na	na
Olefins	na	10.6	9.9	na
Reid vapor pressure (psi)	14.5	7.4	8.5	na
Sulfur (mg/l)	500	338	150	na

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Organic Lead and Manganese

No organic lead in Canadian automotive gasoline after November 1990. In California (1992), rest of USA (1996). In Europe, leaded gasoline was banned in 2000, but many countries implemented the ban earlier, although some were allowed later (Greece? Portugal?). Refer to my article for the dates in specific countries.

MMT was not allowed in unleaded US gasoline after 1980, but allowed in Canadian gasoline (I think still). These parameters are normally identified through GC/ECD.

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Can we determine who manufactured the gasoline??

This is difficult. Gasoline is a fungible commodity; it is bought, sold and traded between the oil companies. For example, because gasoline was found in Chevron's tanks does not mean that Chevron manufactured it. However, sometimes we can estimate who produced the gasoline: for example, the service station across the street from Esso's refinery most likely sells Esso-produced gasoline. But not always!

Now Develop a Model

Take the information from the PIANO analysis, field observations and the known site history, to determine the type of gasoline present, its age and how it was released.

Yup, develop a model….

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An Example

Gasoline, dyed yellow, discovered beneath property that had until recently been undeveloped in Ontario. Before 2004, this was all farmland.

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Background

About 100,000 litres[1] of gasoline were found on the water table beneath the site. Greater than 1 metre of gasoline were detected in some monitoring wells.

Where did it come from and how did it get there??

[1] Based on the dimensions: length, width, thickness & assumed porosity.

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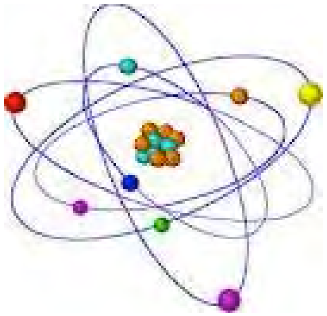
Our Investigation (not only us though)

Monitoring wells were installed by both parties. Soil & groundwater samples collected for laboratory analysis. We also collected four samples of separate-phase gasoline for PIANO analysis. We also performed organic-lead and stable-carbon isotope analyses on the gasoline samples.



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PIANO Results

Based on the ratios: (*iso*-paraffins+naphthenes)/*n*-paraffins and MCH/*n*-C_7, the gasoline is NOT significantly biodegraded. Based on (B+T)/(E+X), B/*cyclo*-hexane and toluene/MCH, there was NOT much dissolution. Based on *n*-pentane/*n*-heptane and 2-methylpentane/2-methylheptane, there was NOT much evaporation.

This gasoline is quite fresh and there's more than 1 metre of it on the water table.

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PIANO Results (Cont'd)

The PIANO results showed that the gasoline was full of *n*-alkanes. The *n*-alkanes are highly biodegradable, but they do not provide much for the octane rating. The octane rating of this gasoline would be about 75 (although this computation is difficult because nowadays the scales do not go below 75!). Either it is a very old gasoline or it was not produced for modern automobiles.

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Organic-Lead Results

Plenty of organic lead. Only tetraethyllead (TEL). No tetramethyllead (TML)[2]. This was a leaded gasoline. But leaded gasoline was banned in Canada as of 1990[1] and the gasoline was quite fresh in 2011, twenty-one years later. But could this gasoline be older than 1990? No. We'll see why in a minute.

[1] By the late 1980s, leaded gasoline was rare in Canada.
[2] TML was very popular in Canada, but less so in the USA (in the 1980s). TML was added until 1990, whereas in the USA it was phased out in the mid-1980s.

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Isotopic Analyses

The isotope analyses: $^{13}C/^{12}C$, showed the same values for all the samples (4). These data suggest that the release was catastrophic[1].

A catastrophic, 100,000-litre release out in the middle of nowhere?

[1] Possible topic for some research? Similar chemical & isotopic composition across the plume = a catastrophic release?? I've been saying this for years, but don't have a reference to back it up.

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So Then, What Is It?

The key is the yellow dye. (I'm color blind. I actually never saw it). The dye means that the gasoline is not taxed.

Farming gasoline was exempted from the organic lead ban and is not taxed in Canada (not taxed as well in the USA and that is possibly where it was manufactured). Considering the octane rating, this gasoline could only be used in tractors. Use of this gasoline in a modern automobile could cause engine damage or at least a large plume of smoke. Hence, we have a farm gas here[1].

[1] This case has not yet gone to court. I should point point out that everyone disagrees with me except for the MOE and, of course, the client (but nobody else considered the gasoline chemistry).

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Gasoline Dyes

The dyes used in petroleum products are normally composed of amines. Hence, they decompose quite readily. Therefore, this gasoline has not been exposed to the environment for too long.

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Why should this case study be important to you? (especially for the students)

Based solely on the hydrogeology (groundwater flow direction), my conclusions would have been entirely different. And before seeing the PIANO and isotopic data, they were. Therefore, for these investigations several (more thane one) different methods should always be employed. Don't base your conclusions on limited data!

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Was the gasoline manufactured to have a low octane rating?

Not necessarily. When I was a kid, the gas station would mix 10% diesel with 90% gasoline when I asked for "lawn-mower gasoline". That is because lawn mowers needed low-octane fuel (just like tractors). It is possible that the gasoline here was a mixture with diesel.

So maybe this gasoline was manufactured in Canada. However, TEL manufacturing in Canada ended in 1994 (The Ethyl Corp. plant in Sarnia closed in 1994).

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Is Organic Lead still available?

Yes. It is still used in aviation gas (propeller planes) and racing gasoline (like NASCAR). Same exception applies in the USA, Europe, Australia and other countries. The organic lead is imported from England[1]. Only TEL is used now. No more TML.

[1] Octel (now known as Innospec) in Port Ellesmere, UK (near Liverpool). There may be other manufacturers in China, but they do not export to North America.

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Would the PIANO Results Here Have Lead Us in the Wrong Direction?

No. The PIANO results informed us that *n*-alkanes were plentiful and, hence, a 75 octane gasoline (or less) was present. I could have deduced a farm gas based solely on the PIANO results (if I was smart!).

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What Do We Learn From This?

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Taylor & Francis

The Rise and Fall of Organometallic Additives in Automotive Gasoline

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Refiners have used numerous gasoline additives since the 1920s to increase automotive performance and correct deficiencies. The history of organometallic additives, in particular lead-, manganese- and iron-containing compounds is discussed. Some of these additives can be helpful to environmental investigators for fingerprinting and age-dating leaded-gasoline releases. Knowing their history, investigators can decipher these releases more efficiently.

Keywords: age-dating techniques, cymantrene, environmental litigation, Ethyl Corporation, ethylene dibromide (EDB), ethylene dichloride (EDC), ferrocene, fingerprinting techniques, gasoline, gasoline additives, groundwater contamination, iron carbonyl, leaded gasoline, methyl cyclopentadienyl manganese tricarbonyl (MMT), mixed leads, tetraethyl lead (TEL), tetramethyl lead (TML), unleaded gasoline

An understanding of the history of gasoline is needed to perform these investigations. In this case, an understanding of the gasoline regulations in Canada was important.

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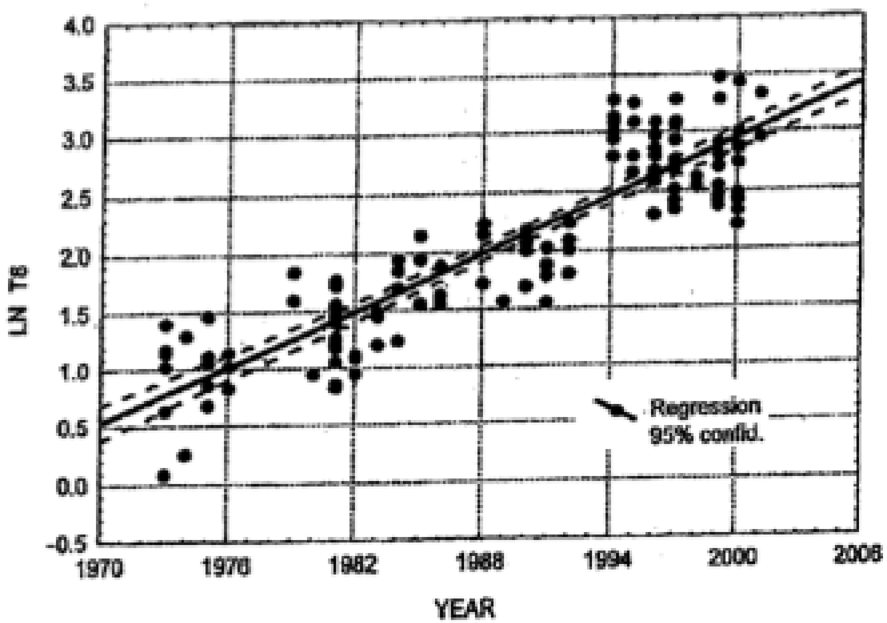
One Needs to Know How the Chemical Composition of Gasoline Changed Over the Years

LN T/8 = natural log of toluene/n-C_8



Source: Schmidt et al, 2003

An example: as organic lead was removed from gasoline, toluene concentrations increased. They may still be increasing because toluene is easy to manufacture.

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Hence, we need to understand:

1. The chemical composition of the gasoline;
2. The site conditions: geology, hydrology and geochemistry, and how it impacted the chemistry of the spilled gasoline (all those ratios);
3. The site history: the locations and conditions of tanks. How many corrosion holes were in the USTs?
4. The horizontal and vertical extent of contamination. If the plume is 2 km long, the leak probably started a long time ago, and
5. The chemical and regulatory history of gasoline in that country/jurisdiction.

These points are the minimum information needed!
Don't try to make conclusions without this information!

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The moral of the story

Consider all of the information:

- Geology;
- Hydrology;
- Chemistry;
- Site history.

René Descartes

This holds true for forensic studies and all scientific investigations.

Questions?

"Let me not answer your question this way..."

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