Tetraethyl Lead Analysis by GC-ICPMS in Support of BC CSR Standards

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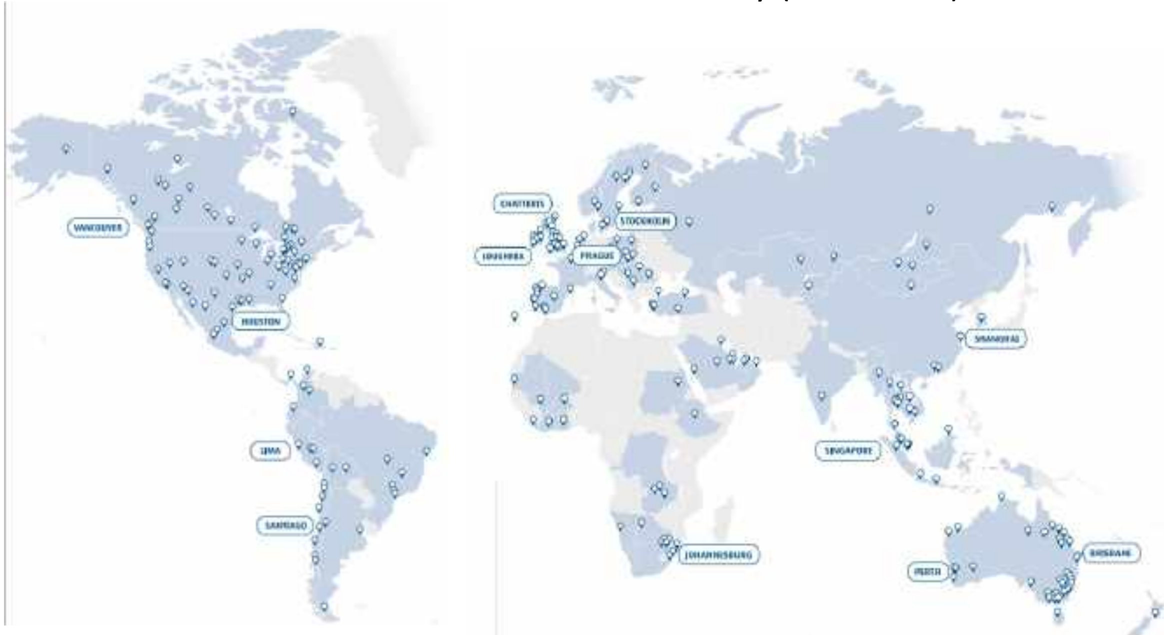
Introduction

ALS Canada Technical Team

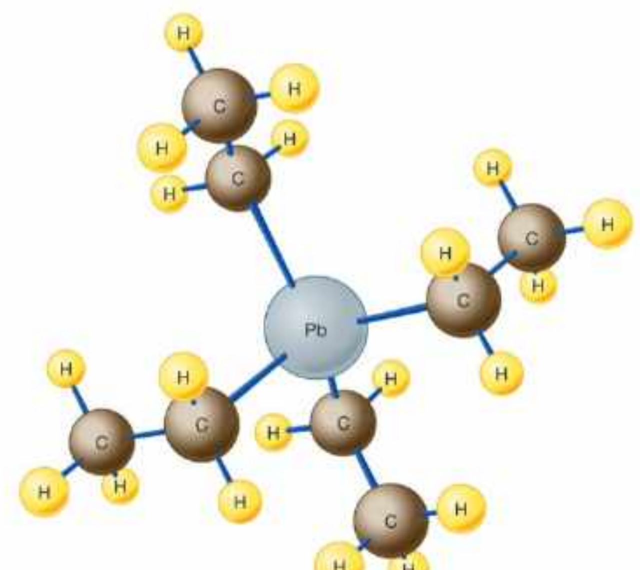
- R&D team across Canada with various fields of specialization.
- My specialization inorganic analysis with a recent focus on speciation and organometallic species.

ALS Burnaby (Vancouver)



Tetraethyl Lead (What is it?)

- Organolead Compound.
- Gasoline additive among other alkyl leads used to increase octane rating.
- Heavier than water.
- Very low solubility in water.
- Highly toxic.



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https://www.britannica.com/science/tetraethyl-lead#/media/1/588986/171067

History

- Toxicity of Pb and TEL eventually forced leaded gasoline to be eliminated.
- Canadian phase-out began 1973, total ban 1990.
- Global total ban 2021. Algeria last hold-out.
- Currently used in Aviation Gas (only TEL as an additive).

Alkyllead compounds found in Gasoline

Analyte	Abbreviation	Boiling point (°C)	Density (D_4^{20})	Water Solubility (mg/L)
Tetramethyl lead	TML	109	2.00	15
Trimethylethyl lead	TMEL	27	1.88	7.65
Diethyldimethyl lead	DEDML	51	1.79	4.6
Methyltriethyl lead	MTEL	70	1.71	1.9
Tetraethyl lead	TEL	200	1.45	0.25

Mixes of Alkyllead compounds used in gasoline

Table 9. *Approximate weight percentage of total lead in individual organoleads for commercial reacted mixes*

	Reacted mixes (RM)		
Organolead	RM25 (%)	RM50 (%)	RM75 (%)
TEL	28.80	4.83	0.09
MTEL	49.51	25.59	3.61
DEDML	18.60	42.40	20.51
TMEL	2.99	23.40	49.60
TML	0.10	3.79	26.19

Table 10. *Approximate weight percentage of total lead in individual organoleads for commercial physical mixes*

	Physical Mixes			
Organoleads	PM10 (%)	PM25 (%)	PM50 (%)	PM75 (%)
TEL	90.0	75.0	50.0	25.0
MTEL	0.00	0.00	0.00	0.00
DEDML	0.00	0.00	0.00	0.00
TMEL	0.00	0.00	0.00	0.00
TML	10.0	25.0	50.0	75.0

Oudijk, Gil(2010) “The Rise and Fall of Organometallic Additives in Automotive Gasoline”, Environmental Forensics, 11: 1, 17-49, First published on: 17 March 2010

- Varied by refinery, process and desired octane.
- Presence of alkyl lead compounds other than TML/TEL can help determine timeline. Usage history of reactive mixes vs physical mixes. Reactive mix use older.
- TML phased out before TEL (mid 80’s)

Alkyllead compounds found in the environment

Class	Abbreviation	
R_4Pb	Me_4Pb Me_3EtPb Me_2Et_2Pb $MeEt_3Pb$ Et_4Pb	Gasoline Source
R_3Pb^+	Me_3Pb^+ Me_2EtPb^+ $MeEt_2Pb^+$ Et_3Pb^+	Degradation
R_2Pb^{2+}	Me_2Pb^{2+} $MeEtPb^{2+}$ Et_2Pb^{2+}	

Source: Stephen J. Hill (2005) "2.10 Speciation of Lead", Handbook of Elemental Speciation II: Species in the Environment, Food, Medicine and Occupational Health. 2005

Toxicity

- General toxicity characteristics from Literature:

1. Toxicity of alkyl lead compounds decrease in the sequence:

$$R_4Pb > R_3Pb^+ > R_2Pb^{2+}$$

2. Methylated species less toxic than ethylated.

Source: Gallert, Claudia & Winter, Josef. (2002). Bioremediation of soil contaminated with alkyllead compounds. Water research. 36. 3130-40.

Degradation and persistence in the environment

- Limited specifics in the literature. Generally, experiments showed a path of de-alkylation ending with inorganic lead.

  R_4Pb » R_3Pb^+ » R_2Pb^{2+} »Pb^{2+}

- Very rapid degradation when exposed to air and sunlight.

Gallert, Claudia & Winter, Josef. (2002). Bioremediation of soil contaminated with alkyl lead compounds. Water research. 36. 3130-40

Persistence in the environment

- Alkyl lead compounds themselves
  - Degrades quickly in sunlight (half-life 2-9 hours).
  - Degrades quickly in water (half-life 2-9 hours surface waters, 2-8 weeks ground water).
  - Degrades quickly in soil (half-life 1-4 weeks).

Source: 1991, Handbook of Environmental Degredation rates. & Ou, LT., Thomas, J.E. & Jing, W. Biological and chemical degradation of tetraethyl lead in soil. *Bull. Environ. Contam. Toxicol.* **52**, 238–245 (1994)

Persistence in the environment

- When contained within a gasoline matrix TEL degradation markedly slower.
- Literature shows a handful of studies now measuring in much longer time periods.
- Consensus in literature: "As long as gasoline hydrocarbons remain in soil, TEL may also remain in soil".

Source: Mulroy, P.T. and Ou, L.-T. (1998), Degradation of tetraethyllead during the degradation of leaded gasoline hydrocarbons in soil. Environmental Toxicology and Chemistry, 17: 777-782.

Forensics applications

- Source of spill.
- Timing of spill.
- Factors such as TEL presence, TML presence, Other alkyl leads (reactive vs physical mix).
- Useful in combination with other corroborating methods.

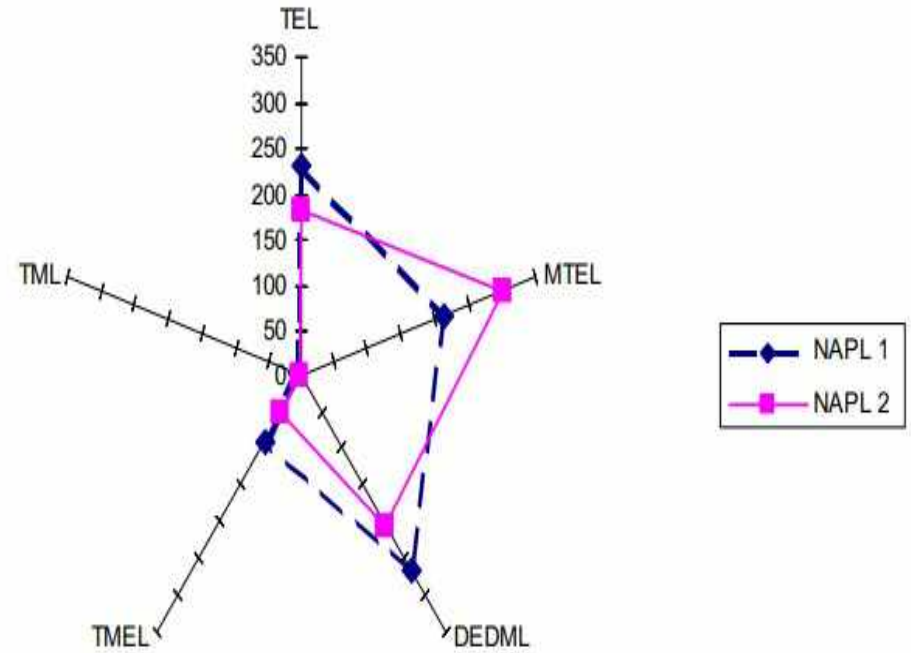


FIGURE 8.12 NAPL alkyllead speciation analysis by direct injection GC/MS provides data that can be used to constrain the age of the release and resolve chemical differences within NAPL samples.

Source: 2015, Introduction to Environmental Forensics third edition

Environmental regulations for Tetraethyl lead

- Most regulations worker exposure related.
  - Many poisonings occurred in the refining of leaded gasoline
  - Worker safety
- Few regulations for water and soil
- BC and ON (Water)
- BC (Soil)

Source: New York Evening Journal, 1924

BC regulations (CSR)

Contaminated Sites Regulation last amended July 7, 2021

SCHEDULE 3.1 – PART 2

GENERIC NUMERICAL SOIL STANDARDS TO PROTECT HUMAN HEALTH[1,2]

COLUMN 1	COLUMN 2	COLUMN 3	COLUMN 4	COLUMN 5	COLUMN 6	COLUMN 7	COLUMN 8	COLUMN 9	COLUMN 10
Substance	Chemical Abstract Service Number (CAS)	Wildlands Natural (WL_N)	Wildlands Reverted (WL_R)	Agricultural (AL)	Urban Park (PL)	Residential Low Density (RL_{LD})	Residential High Density (RL_{HD})	Commercial (CL)	Industrial (IL)
tetrachlorovinphos	961-11-5	600	600	300	600	300	600	1 500	1 500
tetraethyl lead	78-00-2	0.003	0.003	0.0015	0.003	0.0015	0.003	0.025	0.025
tetrahydrofuran	109-99-9	30 000	30 000	15 000	30 000	15 000	30 000	200 000	200 000
tetryl	479-45-8	65	65	30	65	30	65	450	450

GENERIC NUMERICAL WATER STANDARDS[1]

COLUMN 1	COLUMN 2	COLUMN 3	COLUMN 4	COLUMN 5	COLUMN 6
Substance	Chemical Abstract Service # (CAS)	Aquatic Life[2] (AW)	Irrigation[2] (IW)	Livestock[2] (LW)	Drinking Water[3] (DW)
tetrachlorovinphos	961-11-5				6.5[4]
tetraethyl lead	78-00-2				0.001[4,8]
tetrahydrofuran	109-99-9				3 500[4]
tetryl	479-45-8				8[4]

Soils ug/g ; Water ug/L

BC Water Quality Guidelines

British Columbia Working Water Quality Guidelines: Aquatic Life, Wildlife & Agriculture. (Feb 2021)

Table 1 continued. Working water quality guidelines.

Substance[1]	Class	Water Use	Long-term WWQG[2]	Units	Notes	Reference
Imidacloprid	Organic pesticides	Freshwater aquatic life	0.23	µg a.i./L	a.i. - active ingredient; See footnote #9	CCME (2007)
Imidacloprid	Organic pesticides	Marine aquatic life	0.65	µg a.i./L	a.i. - active ingredient; See footnote #9	CCME (2007)
IPBC (3-Iodo-2-propynlbutylcarbamate)	Pesticides	Freshwater aquatic life	1.9	µg/L		CCME (1999a)
Lead - Tetra-ethyl lead	Metals, Organic	Freshwater aquatic life	0.0007	µg/L		Ontario MOEE (1994)
Lead - Tetra-methyl lead	Metals, Organic	Freshwater aquatic life	0.006	µg/L		Ontario MOEE (1994)
Linuron	Organic pesticides	Freshwater aquatic life	7	µg/L		CCME (1995)
Linuron	Organic	Irrigation	3.3	µg/L	Cereals, hay and	CCME (1999c)

Ontario

Ontario Provincial Water Quality Objectives (PWQO) for surface water, 1994

	2,3,5,6-tetrachlorophenol
Tetraethyl lead CAS No. 78-00-2	**0.0007 µg/L (Interim PWQO)[7]**
Tetramethyl lead CAS No. 75-74-1	**0.006 µg/L (Interim PWQO)[7]**

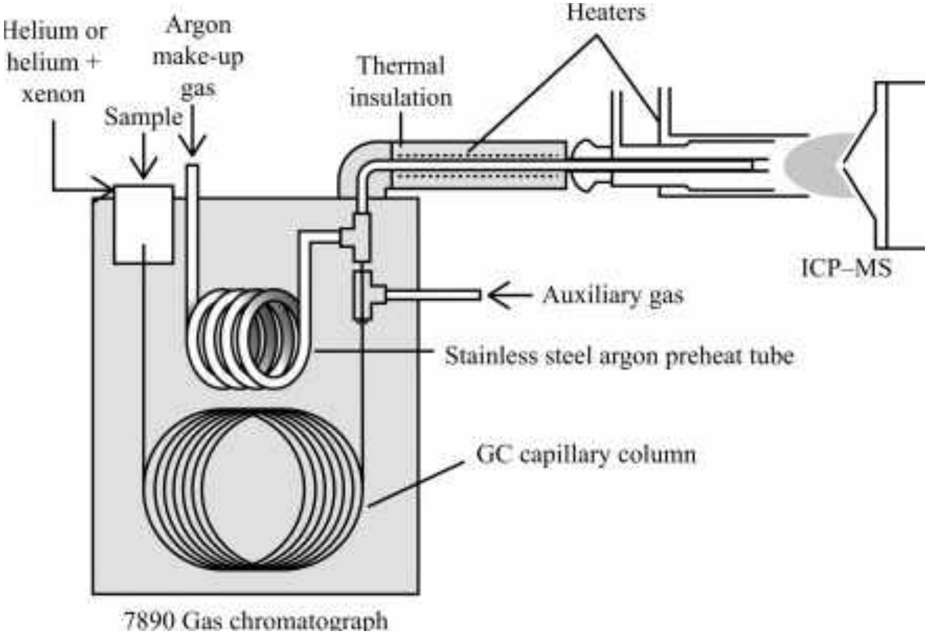
Ontario objectives toxicity based “guide”, not “regulation”.

Analysis Methods for Tetraethyl lead

- Historical Methods
  - GC-MS
    - Poor sensitivity in comparison to guideline needs.
    - Prone to interferences.
- Current (BC lab manual)
  - 2 methods approved for publication, Dec 20, 2019
  - Tetraethyl lead in Soil- PBM : (GC-MS/MS, GC-ICPMS)
  - Tetraethyl lead in Water- PBM: (GC-MS/MS, GC-ICPMS)

ALS Method: GC-ICPMS

GC-ICPMS (Gas Chromatography - Inductively Coupled Plasma Mass Spectroscopy)



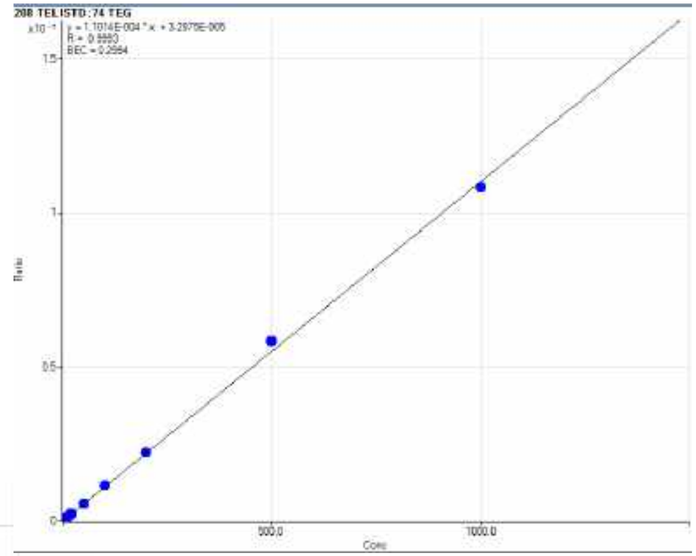
Source: Agilent Technologies

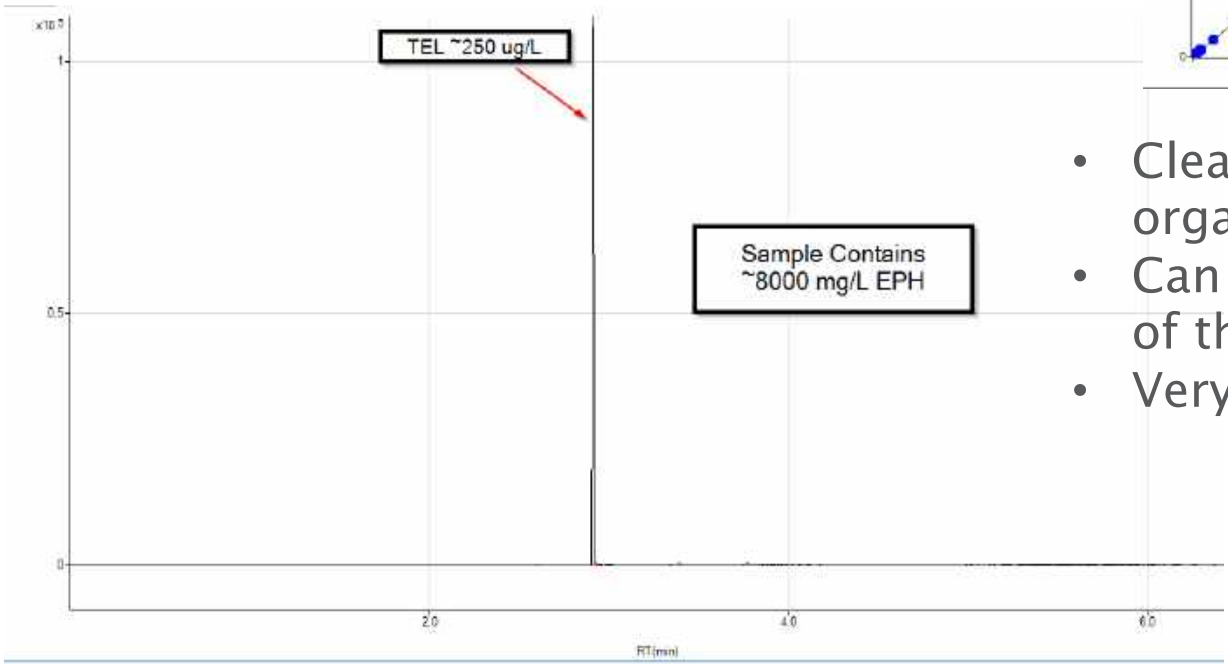
ALS Method: GC-ICPMS

- Use of GC-ICPMS in environmental laboratories extremely rare.
- ALS Burnaby one of only a handful of locations in ALS globally using this technique. Organotins and methyl mercury another application that can use this technique.
- Only laboratory offering this method for tetraethyl lead globally that I can find.
  - Makes sense due to lack of a regulatory drive for analysis.

ALS Method: GC-ICPMS

- Advantages: Why use GC-ICPMS?
  - Unparalleled sensitivity for organometallic compounds.
  - Plasma eliminates all interferences from hydrocarbons in the sample.
  - Very fast analysis compared to GCMS



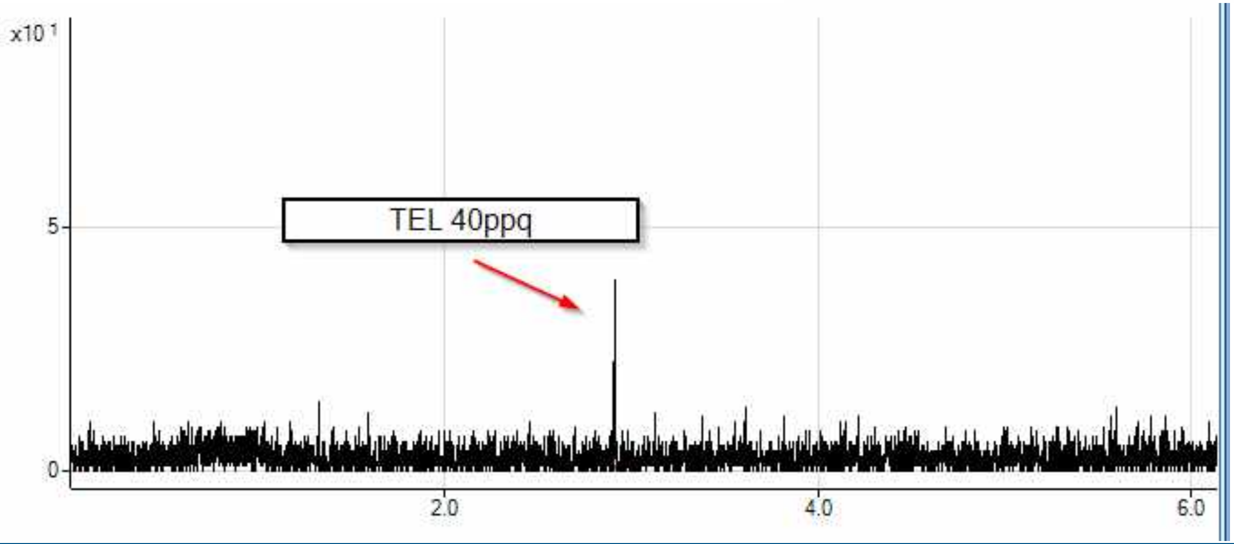


- Clean chromatography. Only organolead compounds.
- Can analyze multiple isotopes of the same element.
- Very linear response.

ALS Method: GC-ICPMS Sensitivity

- BC CSR lowest limit 1.0 ng/L (water). BC/ON WQ 0.7 ng/L
- ALS reporting limit 0.2 ng/L
- 99% MDL <0.05 ng/L (50 ppq!!!)
- Achievable from a single 100mL sample bottle!!

Sampling and Method Details (Waters)	
Sample container	2 x 100 mL amber glass, Teflon-lined septa
Preservation	Sodium Hydroxide (pH>12), pre-charged, zero headspace
Hold time	14 days to extraction, 40 days for solvent extract
Storage Temperature	≤ 6°C (≤ 10°C during transit to laboratory)
Test Method	GC-ICPMS
Limit of Reporting	0.0002 ug/L



GC-ICPMS Challenges

- Challenges
  - Use not widespread. Literature limited.
  - Surrogates and internal standard options more limited in comparison to GC-MS or GC-MS/MS.
    - In our case use tetraethyl tin and tetraethyl germane
  - No spectrum available that could provide structural information to identify unknown peaks outside the presence of the metallic element.

TEL analysis Challenges

- Specific TEL challenges
  - Stability of standards.
  - ALS offering soils shortly. Needed some extra time to address stability of laboratory spikes.
  - Lack of TEL soil reference materials.
  - Additional Organolead compounds difficult to source. TML found and adding soon.

Analysis Summary

- Analysis over the past year:
  - Over 1000 samples analyzed.
  - Best estimate approximately 50 sites in BC.
  - 17 sites observed hits for TEL.
  - ~30% of sites tested contained TEL.

- Observed common characteristics between sites.
  - Petroleum hydrocarbon impacted.
  - Generally, only a fraction of monitoring wells/bore holes at TEL containing sites were positive for TEL.
  - TEL is persistent since we can still find it.
  - However, data seems to indicate in most cases dispersion and prevalence of TEL on particular sites constrained to the hydrocarbon impacted area.

Digging deeper

- Does GC-ICPMS analysis provide any additional value?
- Let's examine 2 case studies I have selected

Case A	Case B
Single site	Collection of sites
No longer operational	Shared history
industrial/heavy machine fueling	Automotive fuel - UST
NAPL contamination underground. Migration of NAPL limited.	Currently operational

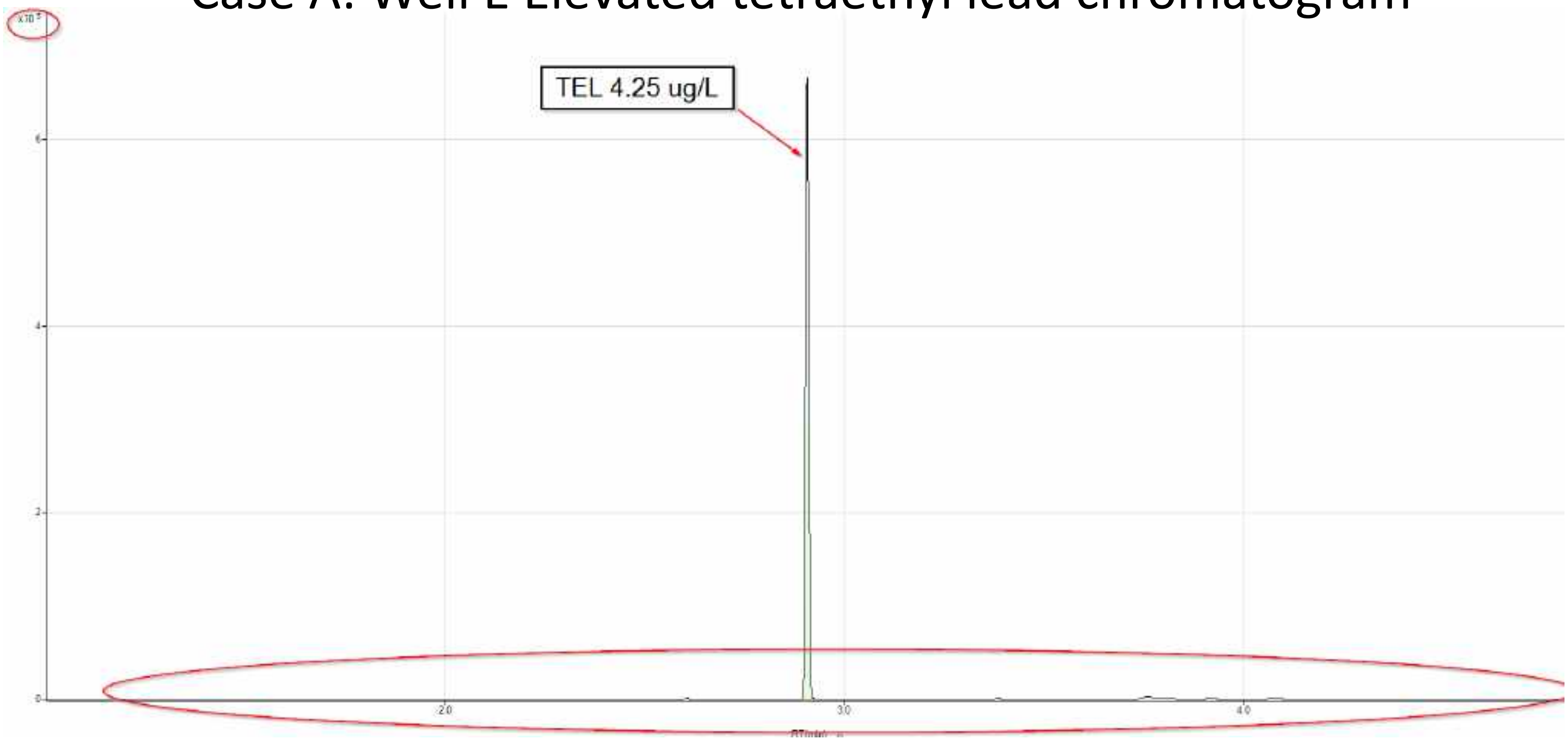
Case A

	TEL (ug/L)	VH(C6-10) mg/L	EPH(C10-19) mg/L
Well A	.396	8160	2620
Well B	0.00128	4500	1160
Well C	0.0001	<100	<250
Well D	Trace	<100	<250
Well E	4.25	8250	2660

- 2 wells similar VH/EPH, differing TEL results.
- Trace PAH's and trace TEL seen in C and D.
- Additional wells not shown TEL non-detect.

Case A

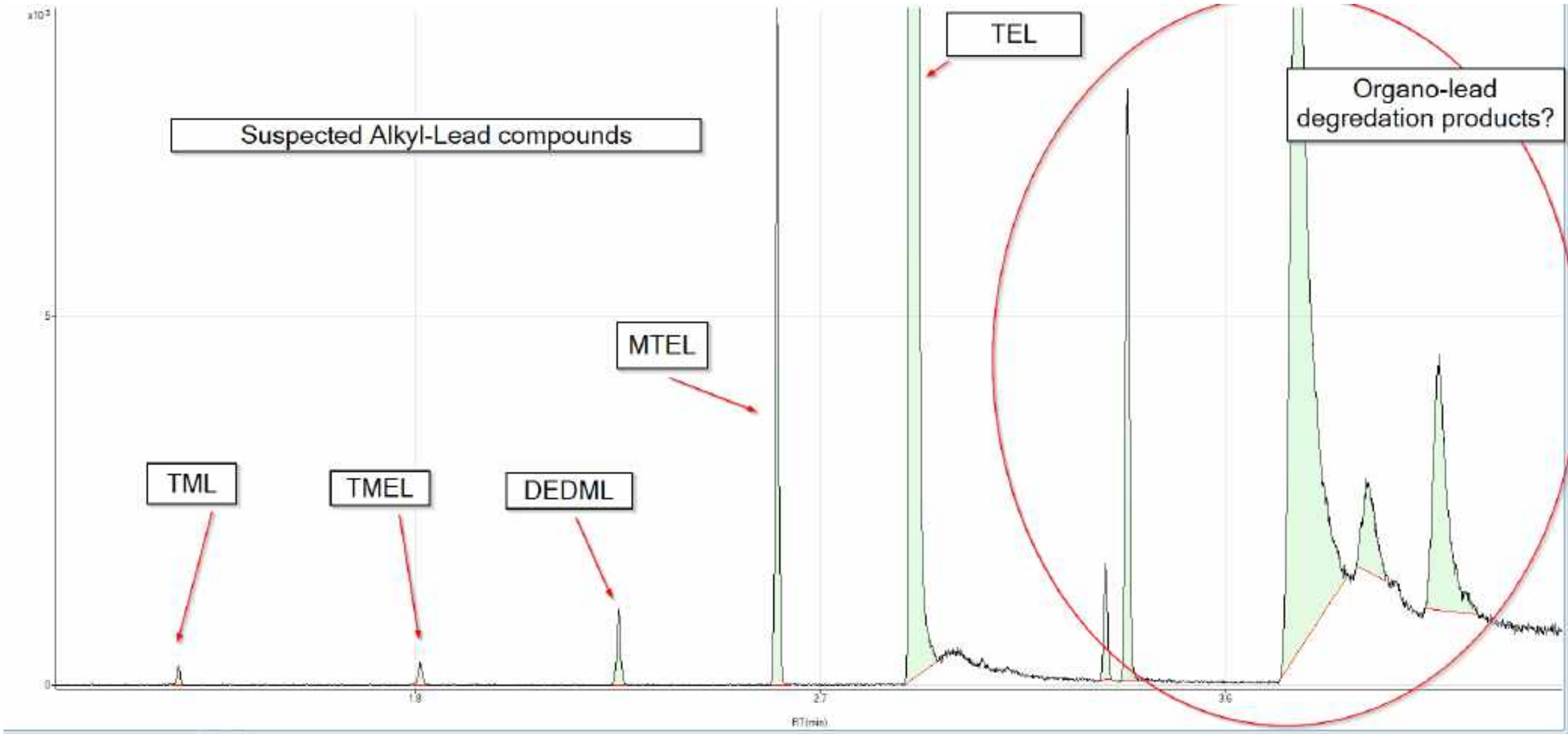
Case A: Well E Elevated tetraethyl lead chromatogram



Can we see any traces of other organo-lead compounds, either other alkyl-leads from gasoline source or degradation products?

Case A

Case A: Well E Elevated tetraethyl lead chromatogram (zoomed 100x)



Case A

- Notable observations
  - Presence of additional alkyl-leads indicates source a “reacted mix”.
  - Wells with similar VH/EPH had differing TEL concentrations.
    - Different plume? Mix?
  - Trace TEL detected where VH/EPH not detected.
  - Complex Pb pattern of both alkyl lead compounds from source and presumed degradation products.
  - TEL component largest of both the alkyl-leads and degradation products.

	TEL (ug/L)	VH(C6-10) mg/L	EPH(C10-19) mg/L
Well A	.396	8160	2620
Well B	0.00128	4500	1160
Well C	0.0001	<100	<250
Well D	Trace	<100	<250
Well E	4.25	8250	2660

Case B

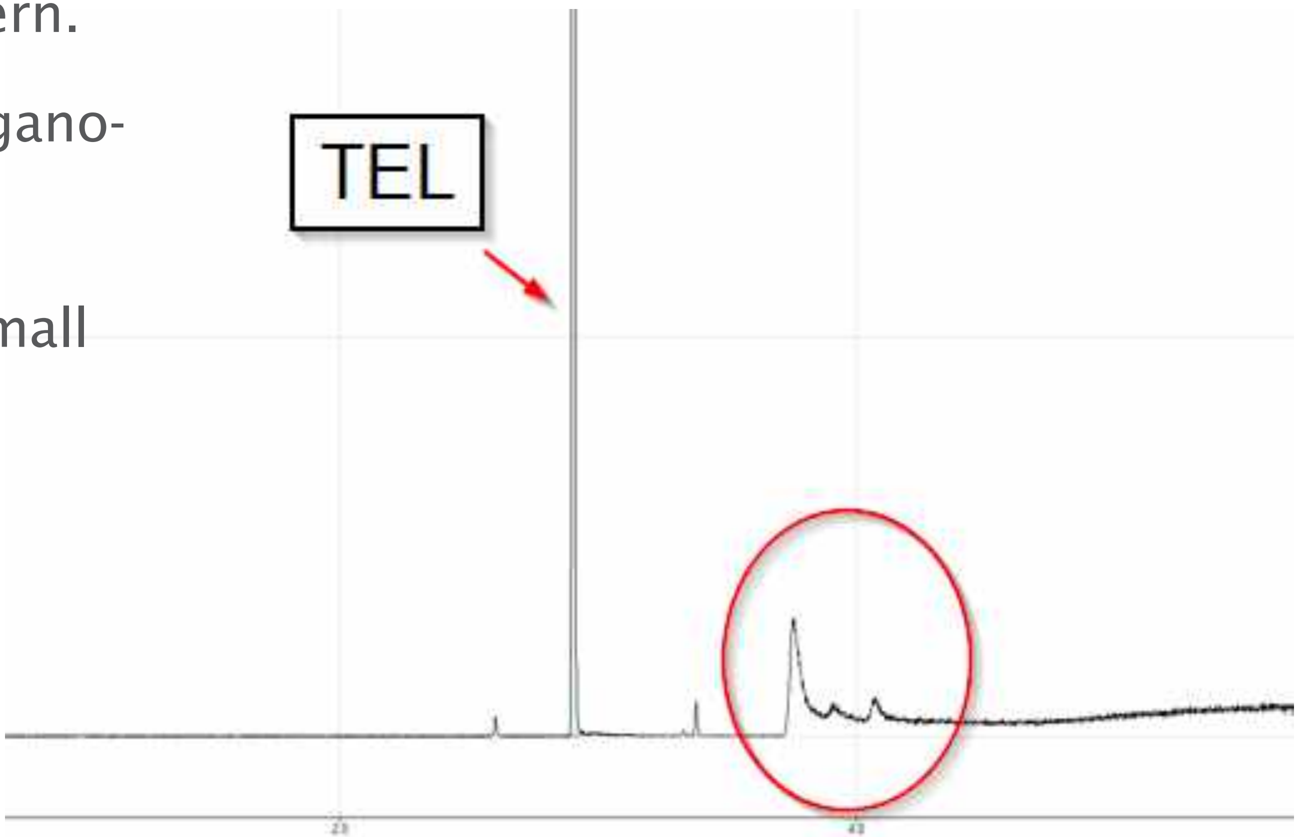
- Multiple sites across BC
- Shared History
- All currently operating sites
- Automotive fuel related

Source: Google maps

Groundwater Sampling

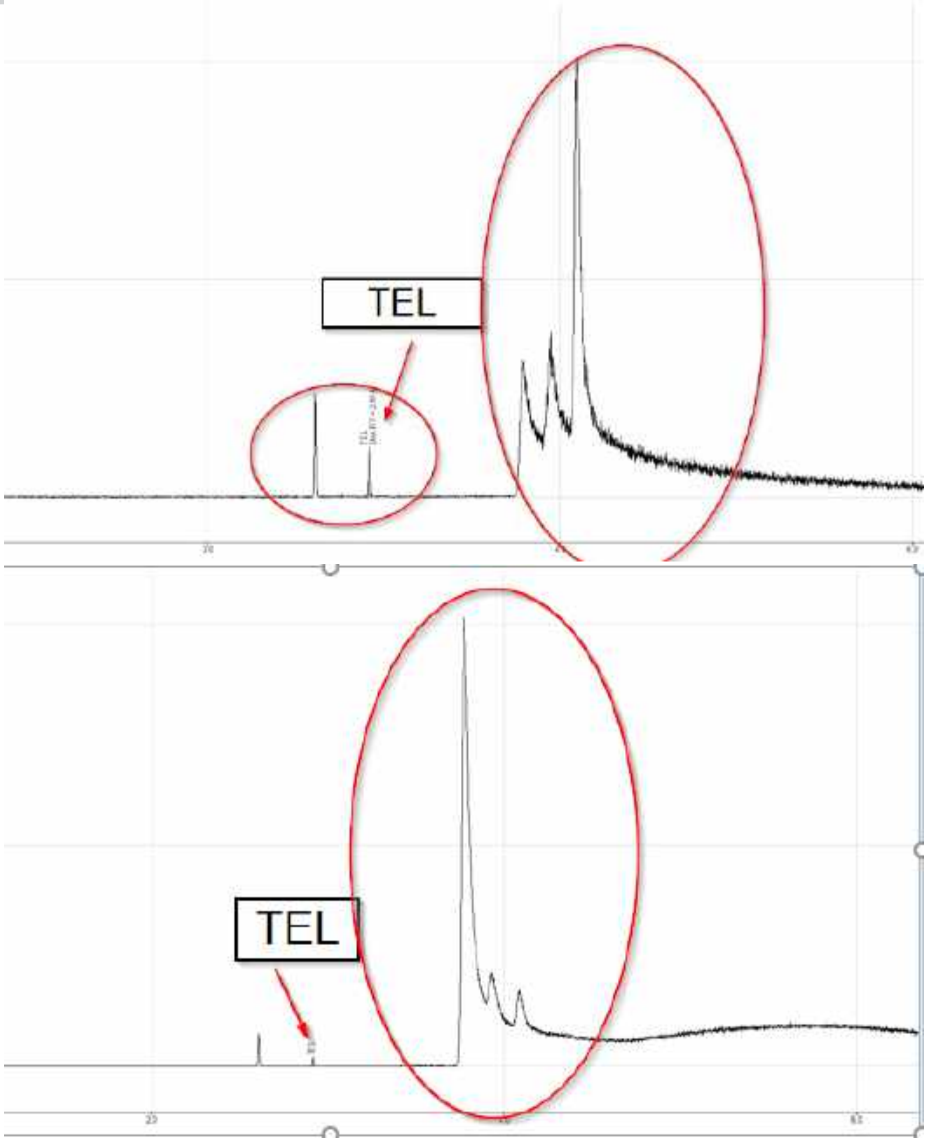
Case B: 3 sites (out of many)

- First example
  - Common pattern.
  - TEL largest organo-lead peak
  - Triplet peak small



Case B: 3 sites (out of many)

- 2 additional sites.
  - Unique patterns
  - TEL smallest peak
  - Triplet shows unique pattern in each.
  - No doublet between TEL and triplet.



Summary: Snapshot of analysis and Case studies

- TEL contamination still present at many sites, some legacy and some still operational.
- TEL generally found within hydrocarbon contamination.
  - Trace TEL may only require trace hydrocarbons to act as a protection against complete degradation.
- TEL contamination tends to be very localized.
  - Possibly expect variation in dispersion depending on site characteristics.
- Additional organolead compounds often present. Patterns observed can be unique to a specific site.
- Degradation path perhaps not as simple as a linear de-alkylation.
  - Further study required

Summary of ALS GC-ICPMS Method

- GC-ICPMS analysis provides highly sensitive analysis well below minimum requirements to meet CSR standards or water quality guidelines.
- GC-ICPMS analysis allows for additional analysis and visualization of organo-lead compounds including alkyl lead compounds from source and degradation products.

Future Work

Near term

– Add TML (tetramethyl lead) to support water quality guidelines.

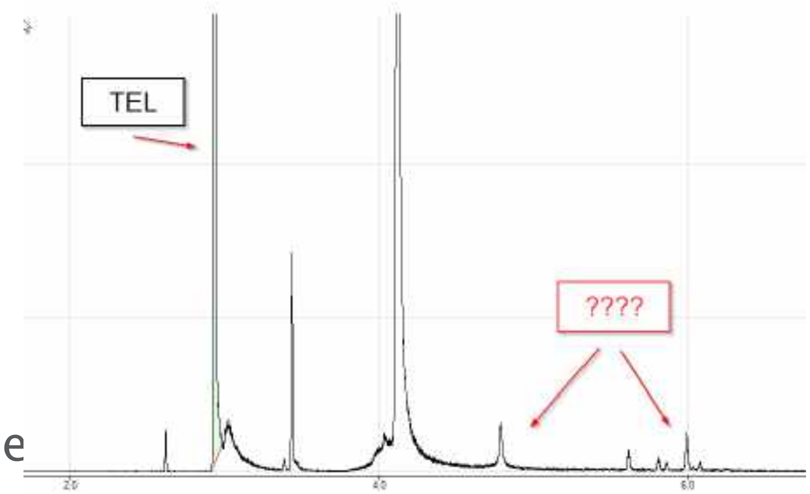
– Characterize TEL results vs T/D Pb.

Longer term

– Identify additional the organo-leads including degradation compounds

– Add additional metal elements to the TEL scan. May provide information on other additives (Mn, Fe, S) .

Recent submission: Always something new!!



Thank you and any Questions?

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