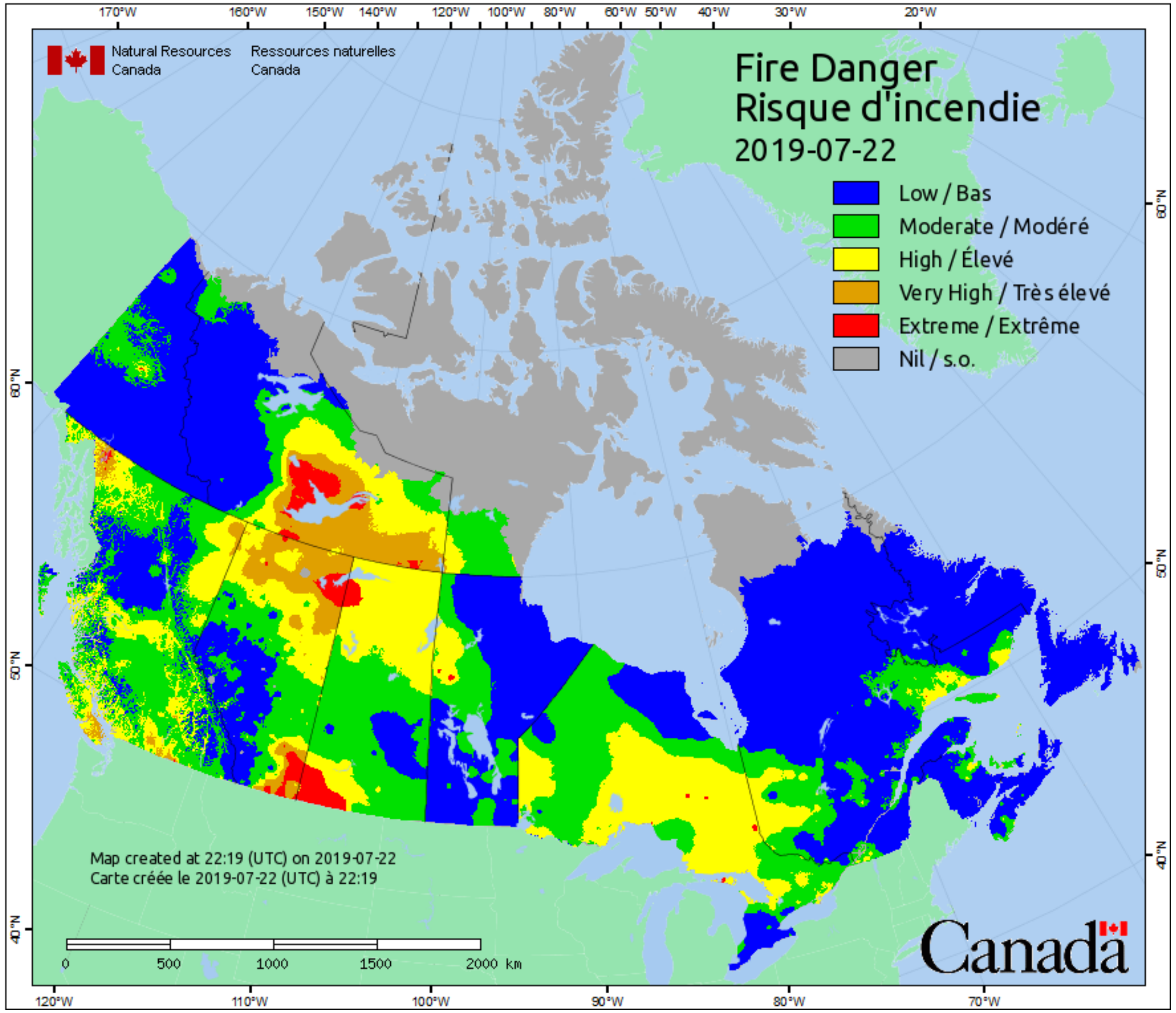
From Wildfire Origins to Courtroom Verdicts:

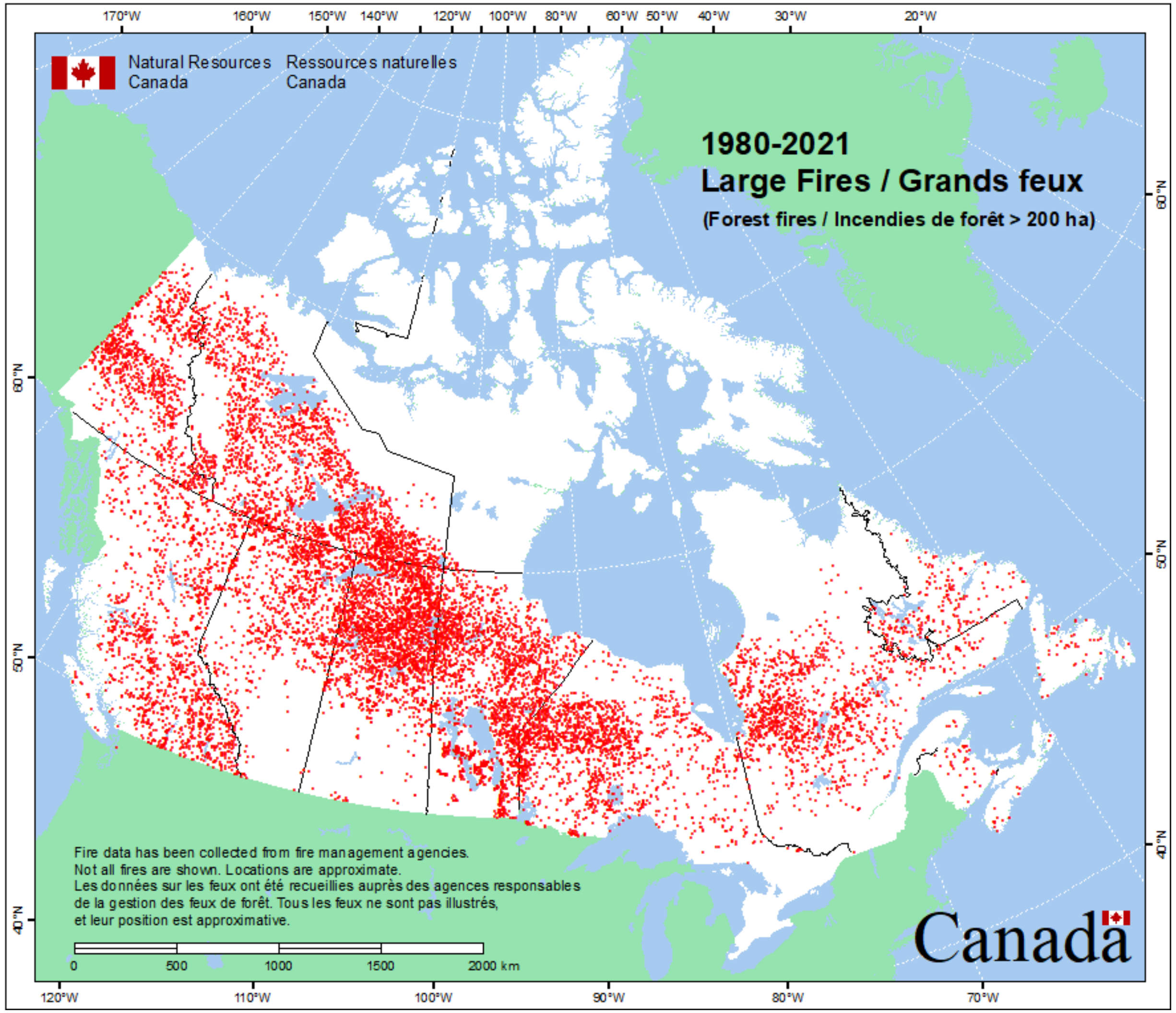
Exploring Arson Investigations with Multidimensional Chromatography

Fire Danger

How easy it is to ignite vegetation, how difficult a fire may be to control, and how much damage a fire may do



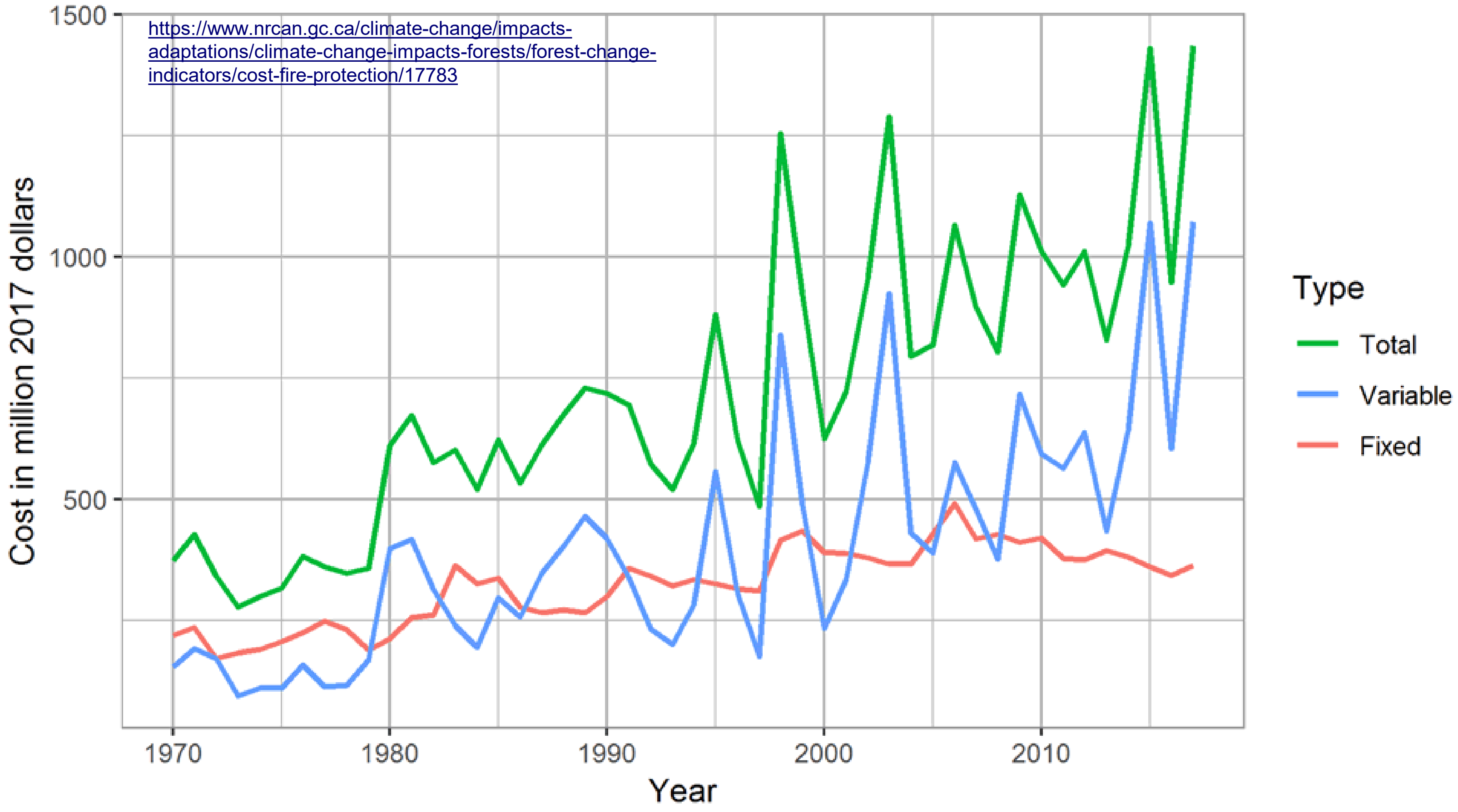
Types and scale of fire incidents



8000 fires occur each year, and burn an average of over 2.1 million hectares

these represent a small percentage of all fires but account for most of the area burned (usually more than 97%).

Cost of fighting fires in Alberta



Agencies plan budgets based on average wildland fire suppression costs over a period of several years. However, fire activity. and severity varies considerably from year to year, making it difficult to anticipate future costs.

The annual national cost of fire protection **exceeded $1 billion for six of the last 10 years**. On average, costs have **risen** about **$150 million** per decade since data collection started in 1970

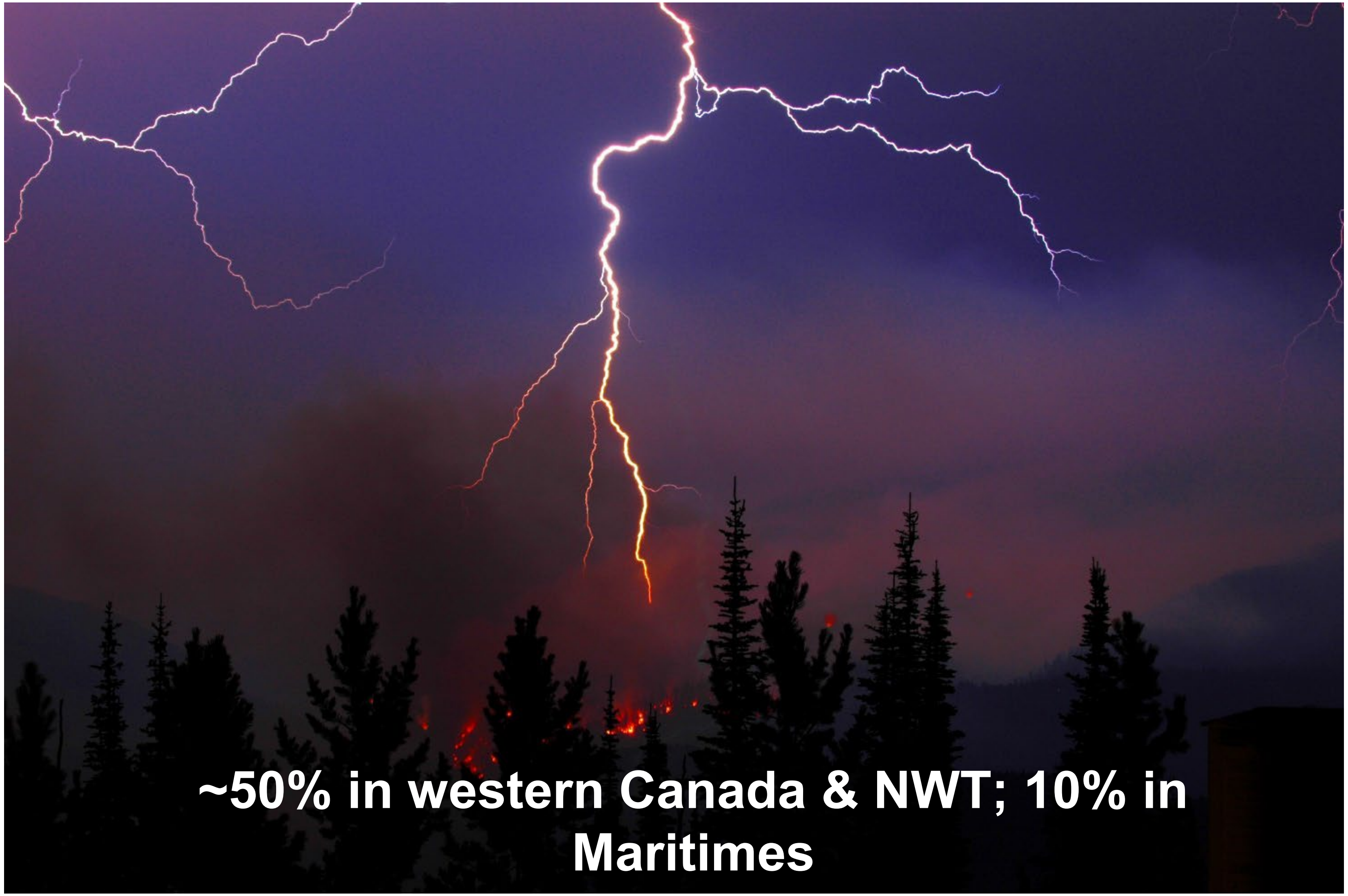
Types and scale of fire incidents

Type of fire incident[3]	2017	2018	2019	2020	2021
	Number				
Total fire incidents	33,026	36,428	33,749	35,495	39,047
Total structural fires[4]	15,843	16,272	15,641	15,168	15,986
Residential fires[5]	10,557	10,862	10,397	10,338	10,819
Industrial fires[6]	633	637	697	630	607
Assembly fires[7]	925	855	860	670	692
Mercantile fires[8]	593	590	615	586	591
Business use/personal service fires[9]	256	259	237	245	256
Institutional fires[10]	356	323	325	251	283
Storage property fires[11]	936	989	949	947	1,004
Other structure type[12]	1,587	1,757	1,561	1,501	1,734
Vehicle fires[13]	5,904	6,235	5,795	5,428	5,155
Outdoor fires[14]	11,055	13,625	11,553	14,361	17,084
Unknown type of fire incident	224	296	760	538	822

How do they start?

In Canada, two-thirds of all forest fires are **caused by people**, while lightning causes the remaining third

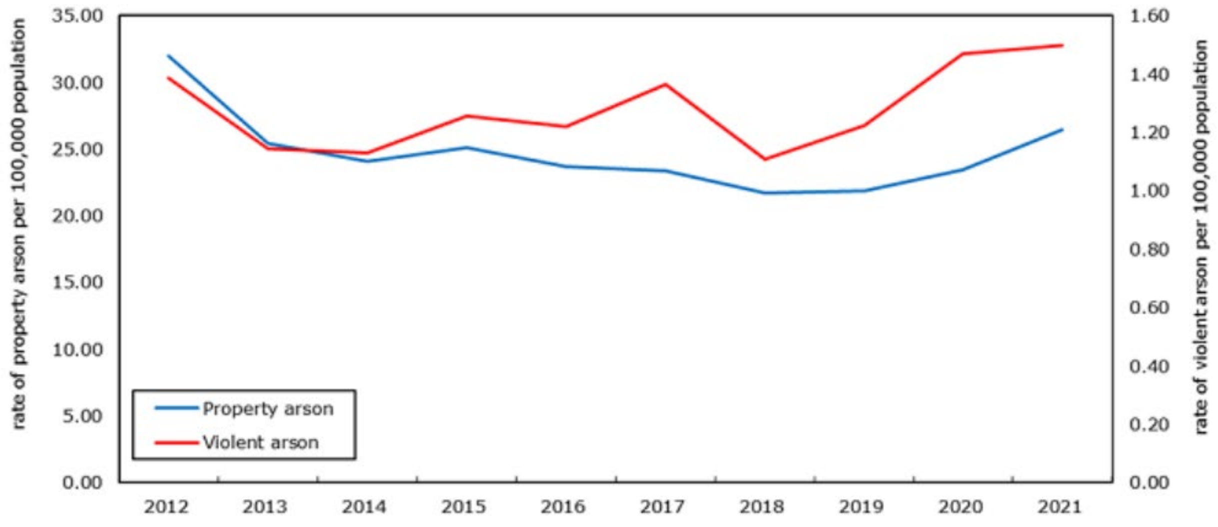
lightning fires account for over 85% of the area burned in Canada – remote, challenging to suppress



Human Caused

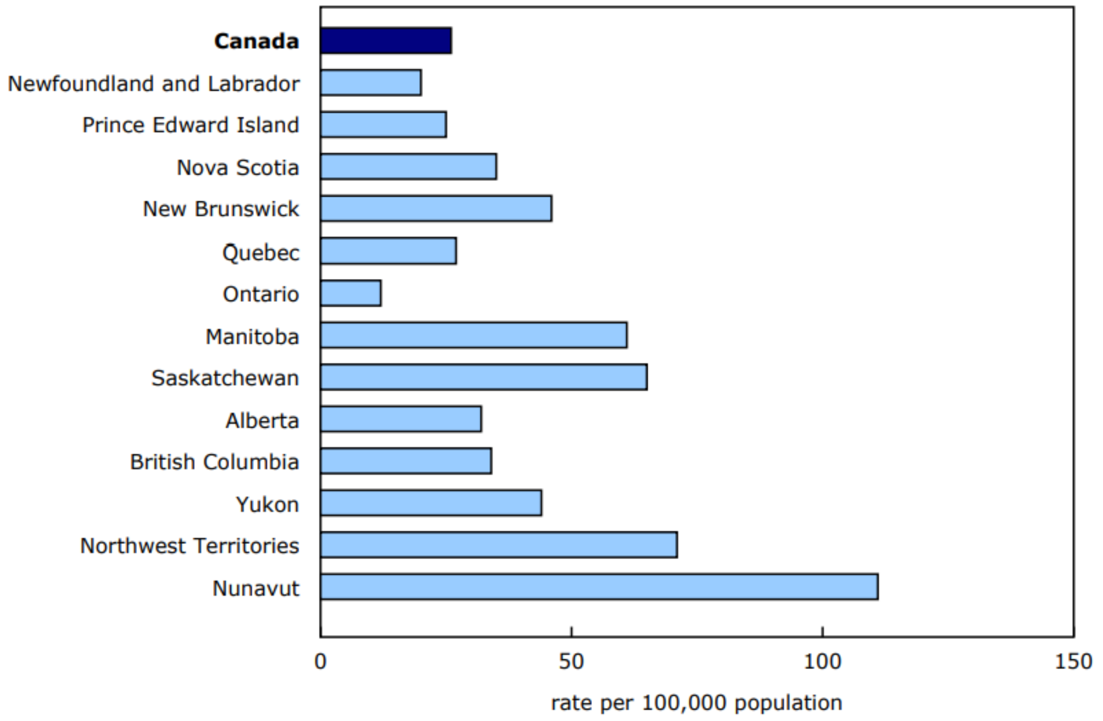
Human-caused fires usually start close to communities, where they are reported quickly and dealt with by local fire crews

Police-reported arson and fire-related homicide in Canada



Incidents in the rural north are 2.5x higher than the rate in the rural south and 4x times higher than that in urban areas

2012 to 2021, Canadian police services reported nearly 95,000 incidents of arson 95% of them were for arson solely related to property (property arson), while the remaining 5% were for arson with a disregard for human life (violent arson)

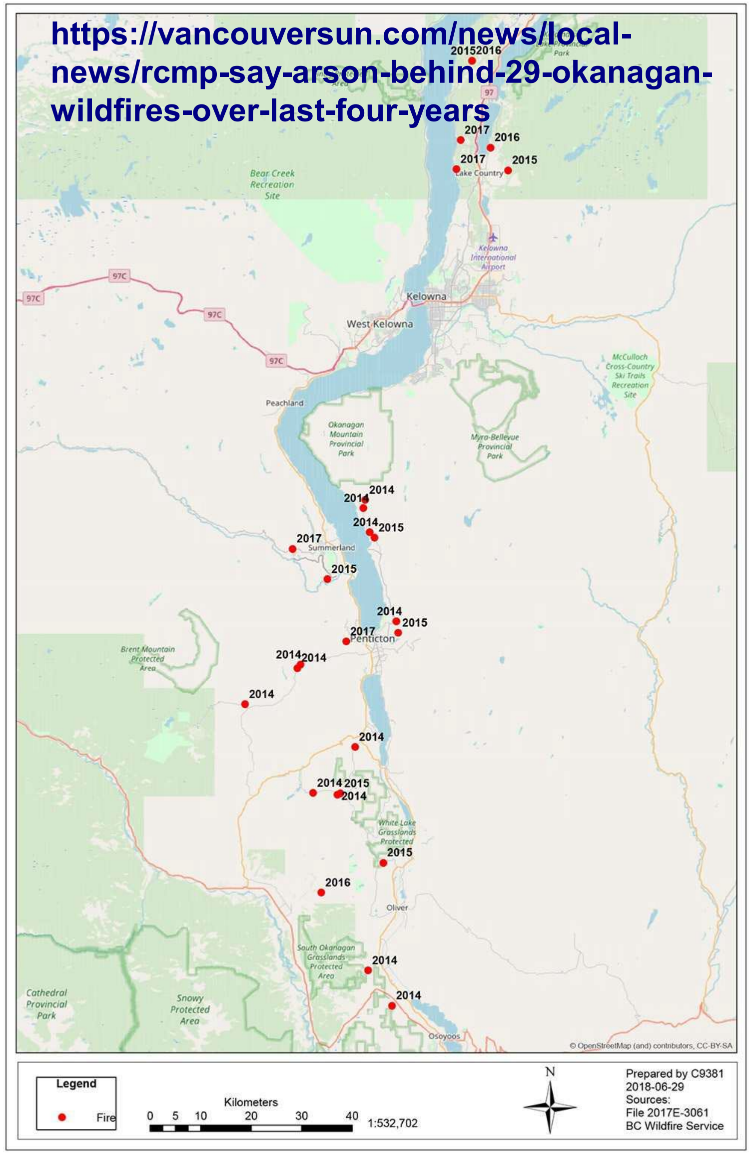


Arson

Five youths between the ages of 12 and 15 have been arrested – fire set near school

https://globalnews.ca/news/5334842/five-youths-age-12-15-arrested-by-little-grand-rapids-rcmp-for-arson/

https://vancouversun.com/news/local-news/rcmp-say-arson-behind-29-okanagan-wildfires-over-last-four-years



interface' settings rural setting with buildings

RCMP created a task force to identify the person — or persons — responsible for the wildfires.

Arsonist: Who are they?

Age, sex, motivation, employment, mental health;

more likely to occur on weekend, evening or night (6pm-6am), spring and summer (60% April - September)

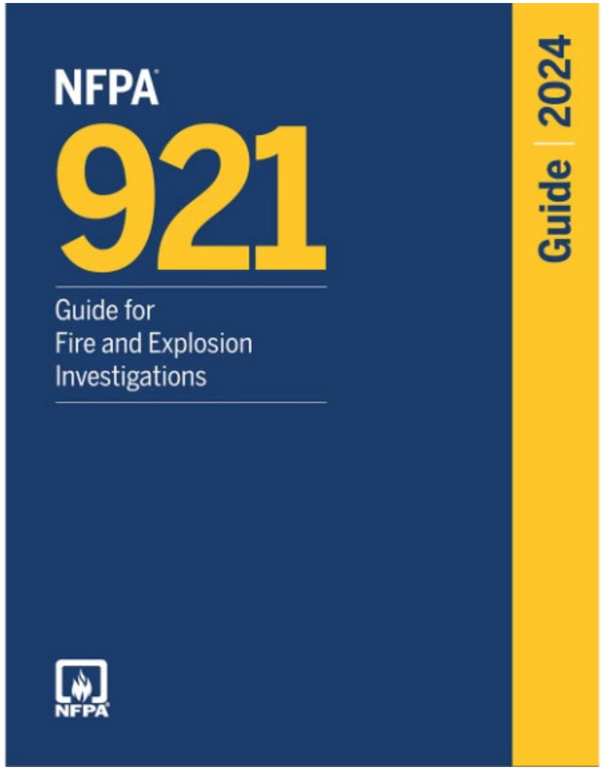
Urban or Rural - almost always exclusively men ranging in age from 18 to 30 who enjoy the outdoors, have jobs and set fires near where they live

Origin to Courtroom

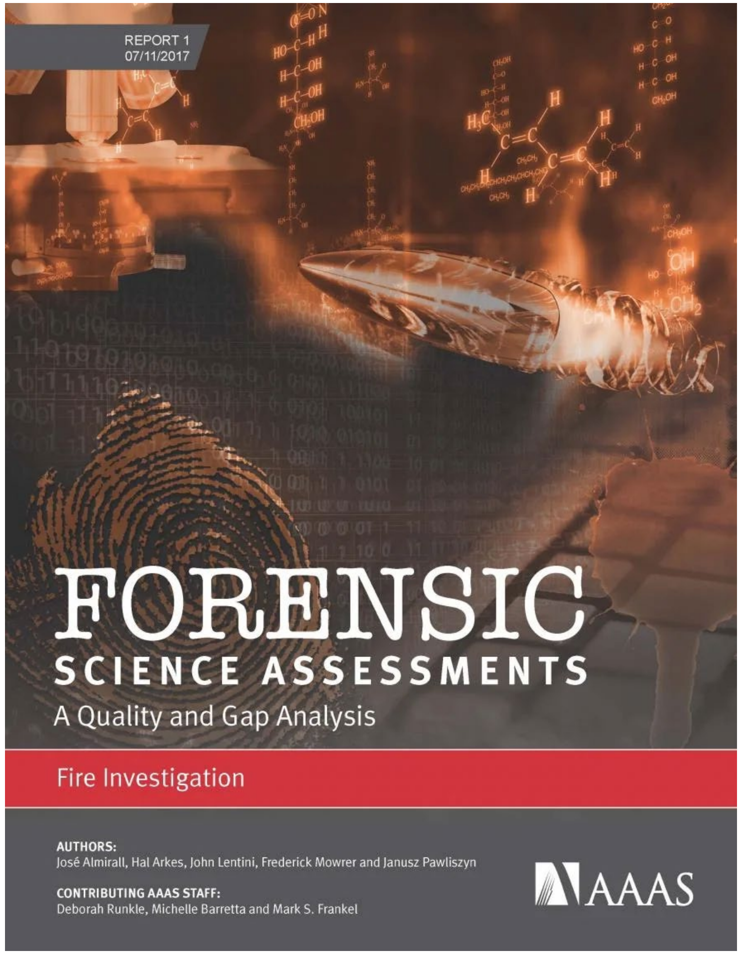
Challenges of Fire Investigation

Challenges, Knowledge gaps, Progress

National Fire Protection Association (first 1992)

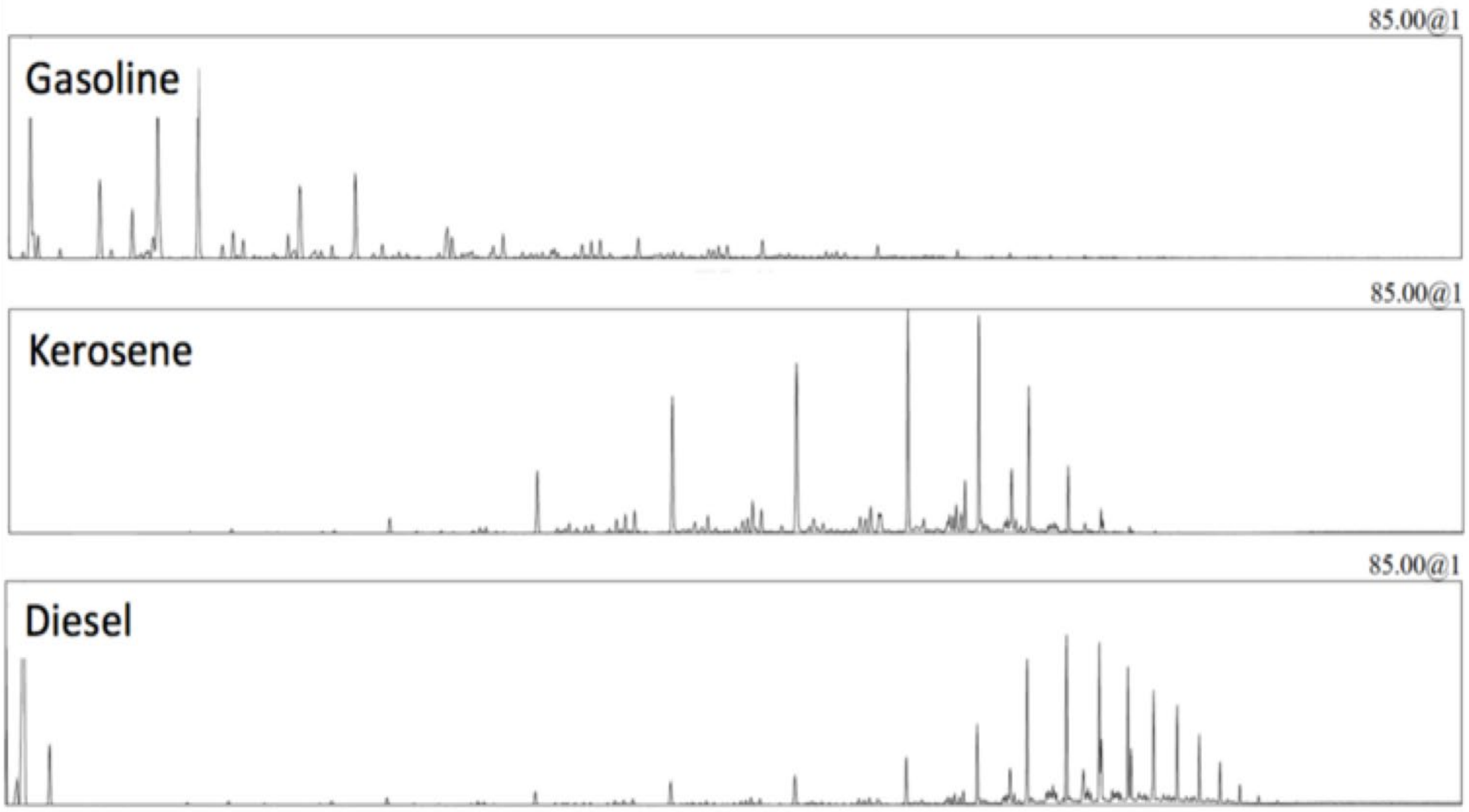


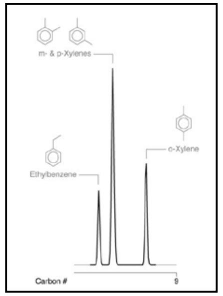
ASTM E1618 - 1997



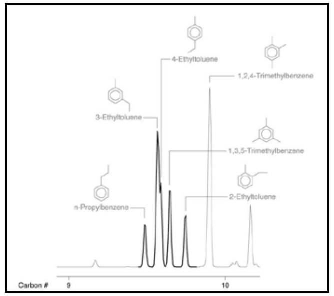
American Association for Advancement of Science (2017)

ILR Analysis ASTM 1618-19

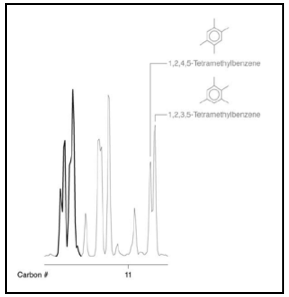




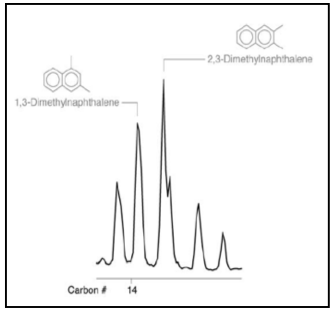
Three Musketeers
C2-benzenes



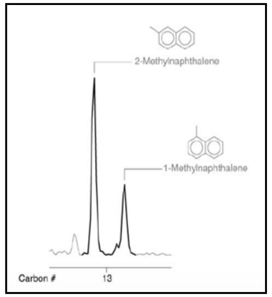
Castle Group
C3-benzenes



Gang of Four
C4-benzenes

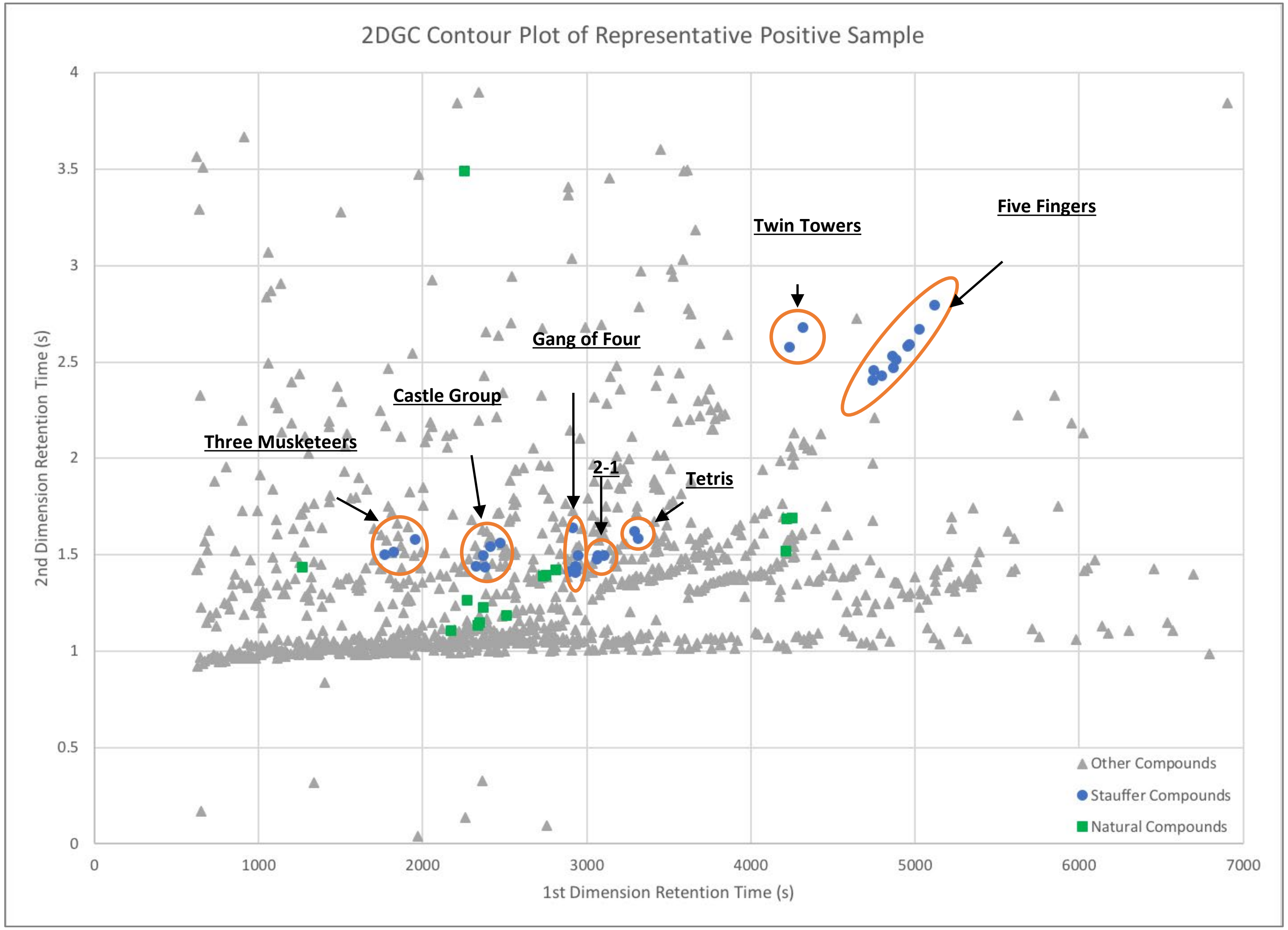


Five Fingers
C2-naphthalenes



Twin Towers
C1-naphthalenes

Potential Of GC x GC



Method Development

Journal of Chromatography A 1656 (2021) 462495

Contents lists available at ScienceDirect

Journal of Chromatography A

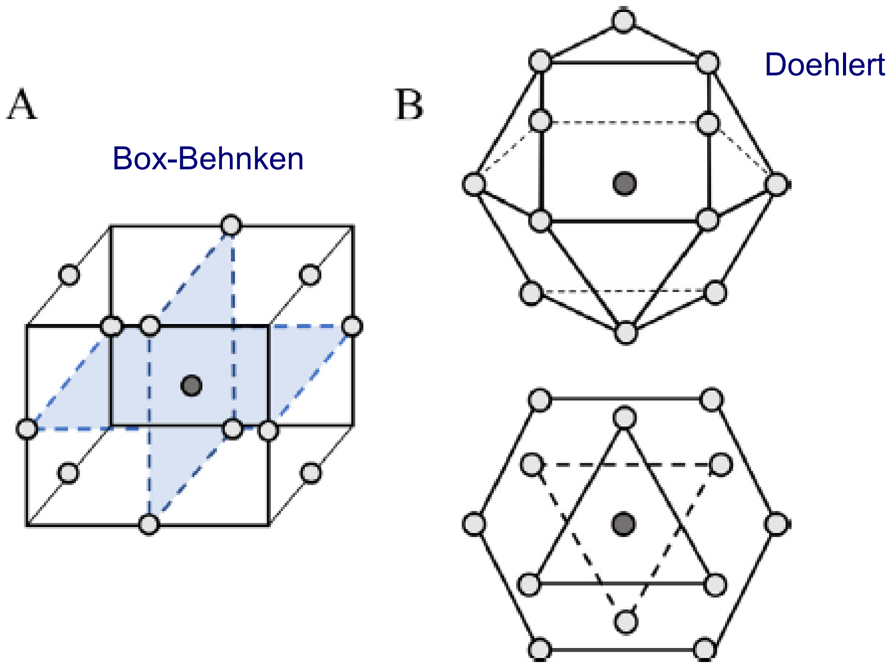
journal homepage: www.elsevier.com/locate/chroma

ELSEVIER

Method development for optimizing analysis of ignitable liquid residues using flow-modulated comprehensive two-dimensional gas chromatography

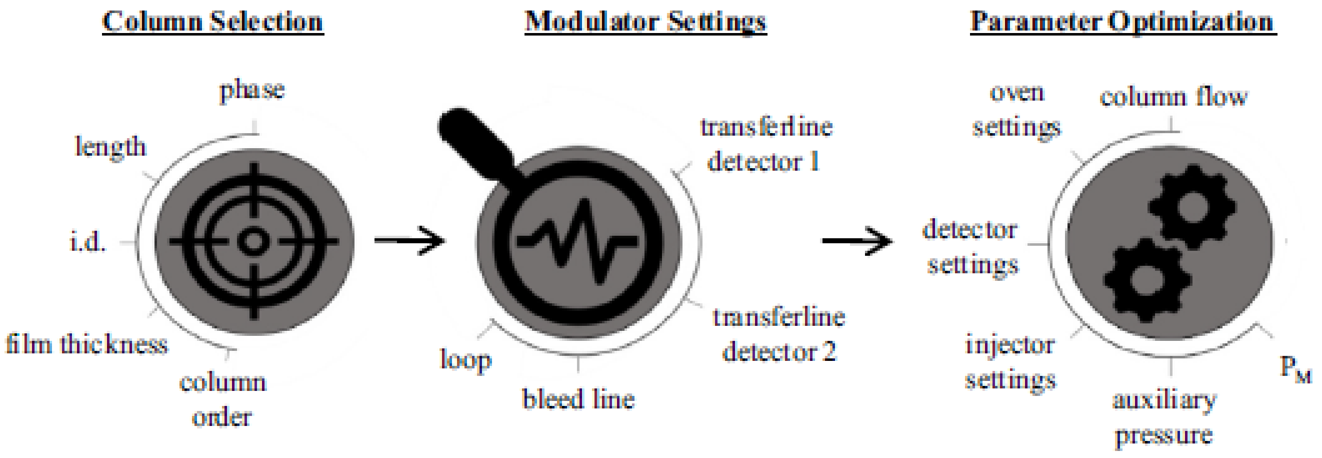
Nadin Boegelsack[a,b,*], Kevin Hayes[a,c], Court Sandau[a,d], Jonathan M. Withey[e], Dena W. McMartin[b], Gwen O'Sullivan[a]

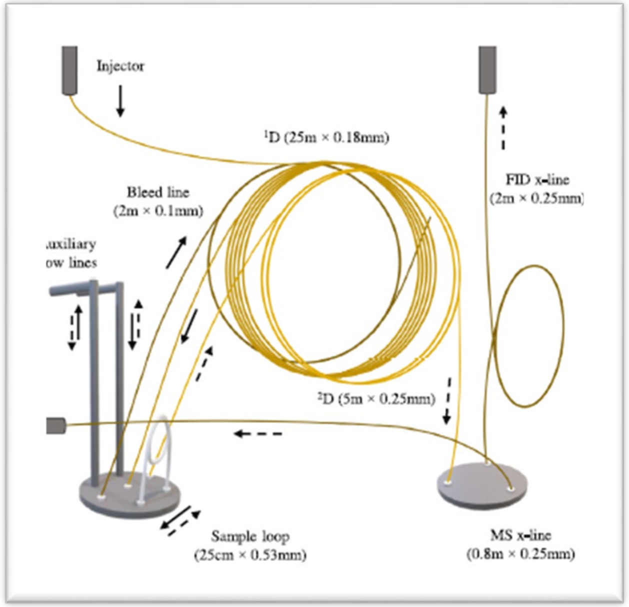
[a] Department of Earth and Environmental Sciences, Mount Royal University, 4825 Mount Royal Gate SW, Calgary, AB Canada, T3E 6K6
[b] Department of Civil, Geological and Environmental Engineering, University of Saskatchewan, 57 Campus Drive, Saskatoon, SK Canada, S7N 5A9
[c] Manchester Metropolitan University, Ecology & Environment Research Centre, Chester Street, Manchester, U.K., M1 5GD
[d] Chemistry Matters Inc., 104-1240 Kensington Rd NW Suite 405, Calgary, AB Canada, T2N 3P7
[e] Department of Chemistry and Physics, Mount Royal University, 4825 Mount Royal Gate SW, Calgary, AB Canada, T3E 6K6



Method development undertaken to fully utilize the potential of GC ×GC by maximizing separation space and resolution

Study Design





Elements to consider:
Selectivity, Retention, Resolution, Peak Capacity / Area Usage, Peak Shape

Achieved by:
Stationary Phase Chemistry, Column Dimensions, Orthogonality

Elements to consider:
Sensitivity, Peak Skewing / Amplitude, Carbon Loading, Dilution Effect

Achieved by:
Flow Ratio, Loop Fill, Detector Efficiency

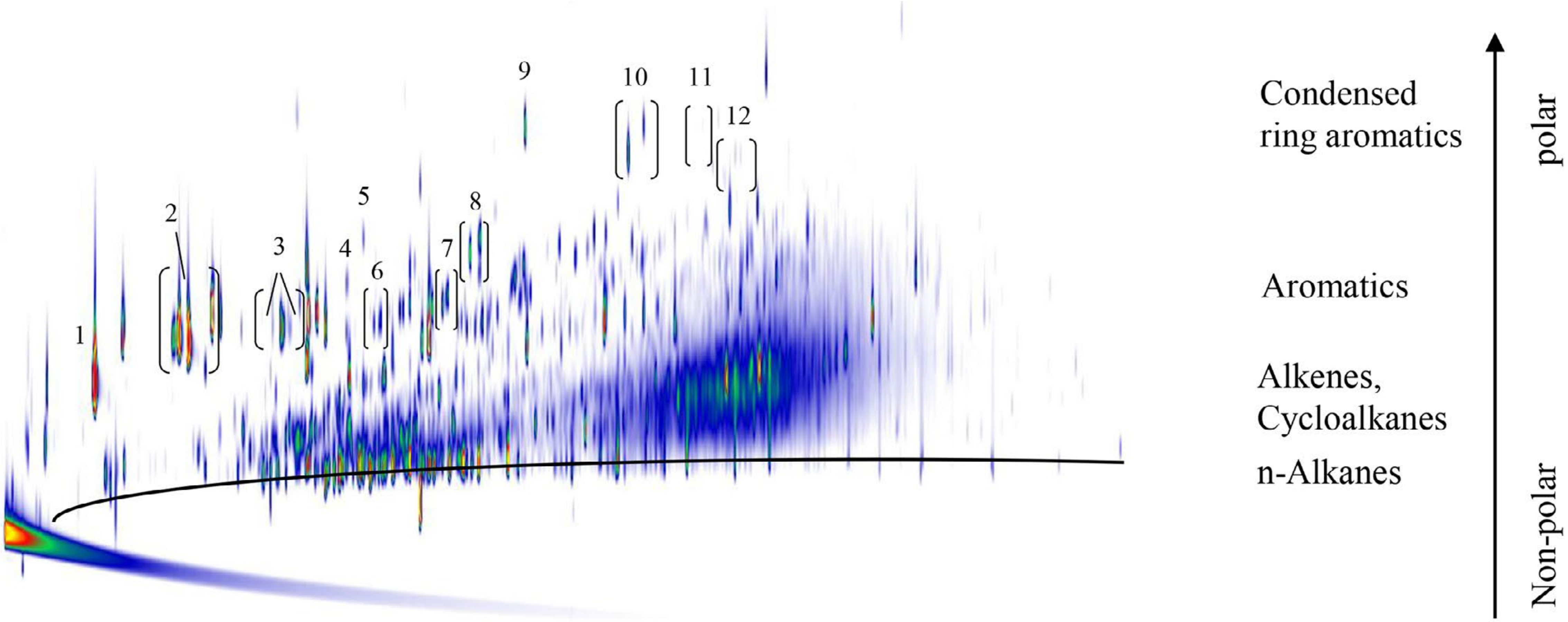
Elements to consider:
Sensitivity, Selectivity, Retention, Resolution, Peak Capacity / Area Usage, Peak Shape, Wraparound

Achieved by:
Oven Programming, Inlet Pressure (Column Flow), Modulation Period

Seven column combinations with different stationary phase chemistry, column dimensions and orthogonality were assessed for suitability based on target compound selectivity, retention, resolution, and peak shapes, as well as overall peak capacity and area use

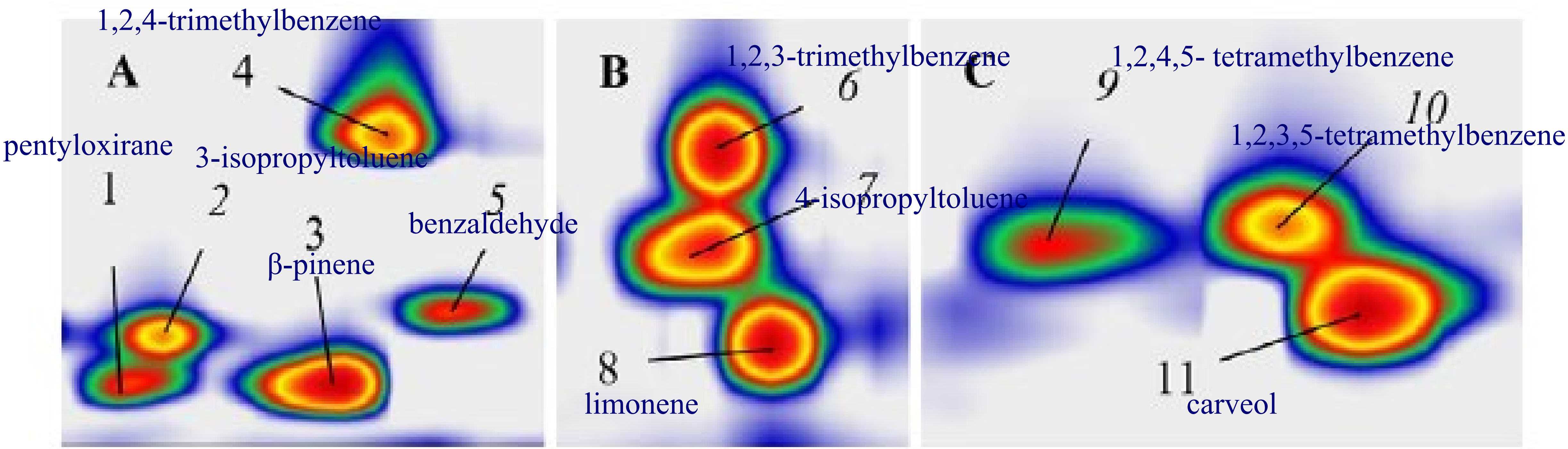
Wildfire Debris Sample

The final method employed a low polarity column (5% diphenyl) coupled to a semi-polar column (50% diphenyl)



Certified reference standards and simulated wildfire debris were used for method development and verification, and wildfire debris case samples scrutinized for method validation

Wildfire matrix interferences



The resulting method was evaluated against ASTM E1618 and found to be an ideal routine analysis method providing great resolution of target com- pounds from interferences and excellent potential for ILR classification within a complex sample matrix.

Retention Time Indices

Journal of Chromatography A 1635 (2021) 461717

Contents lists available at ScienceDirect

Journal of Chromatography A

journal homepage: www.elsevier.com/locate/chroma

ELSEVIER

Development of retention time indices for comprehensive multidimensional gas chromatography and application to ignitable liquid residue mapping in wildfire investigations

Nadin Boegelsack[a,b,*], Court Sandau[a,c], Dena W. McMartin[b], Jonathan M. Withey[d], Gwen O'Sullivan[a]

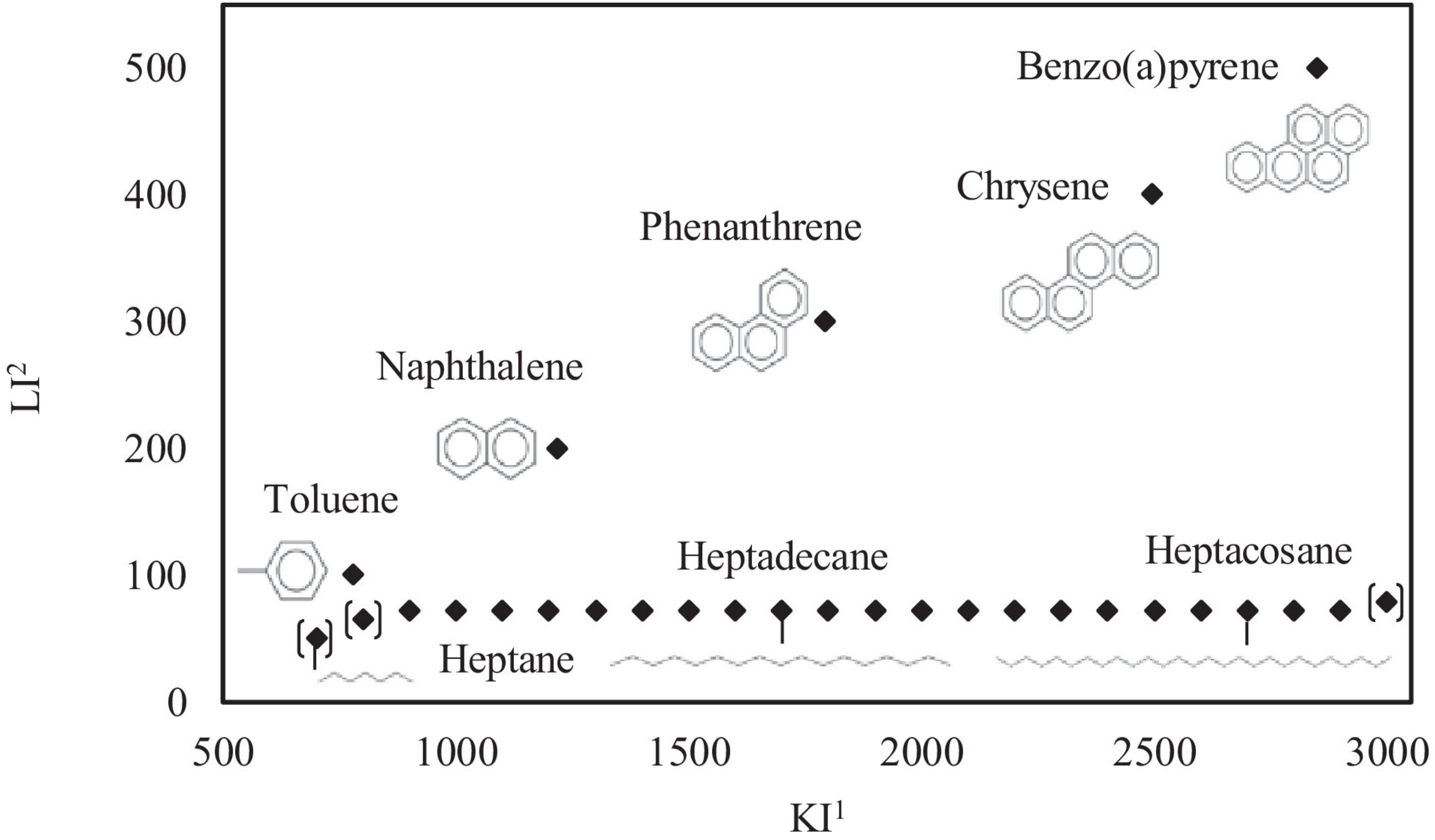
Kovats indices

$$KI^1 = 100n + 100\left(\frac{t_x - t_n}{t_{n+1} - t_n}\right)$$

Lee indices

$$LI^2 = 100\left(\frac{t_x - t_n}{t_{n+1} - t_n}\right)100z$$

Applied a combination of two well-established GC RI systems: non isothermal Kovats index in the first dimension and Lee index in the second dimension



KLI retention index for calibration compounds highlighting the relationship between increasing carbon number (first dimension) and number of aromatic rings (second dimension). Brackets highlight heptane, octane and triacontane as com- pounds outside of linear alkane alignment.

KLI RI system showed very good correlations when compared with predicted values and existing RI systems (r2 = 0.97 in first dimension, r2 = 0.99 in second dimension) and was valid for a wide range of analyte concentrations and operational settings (coefficient of variance (CV) < 1% in first dimension, < 10% in second dimension).

ILR mapping according to ASTM E1618

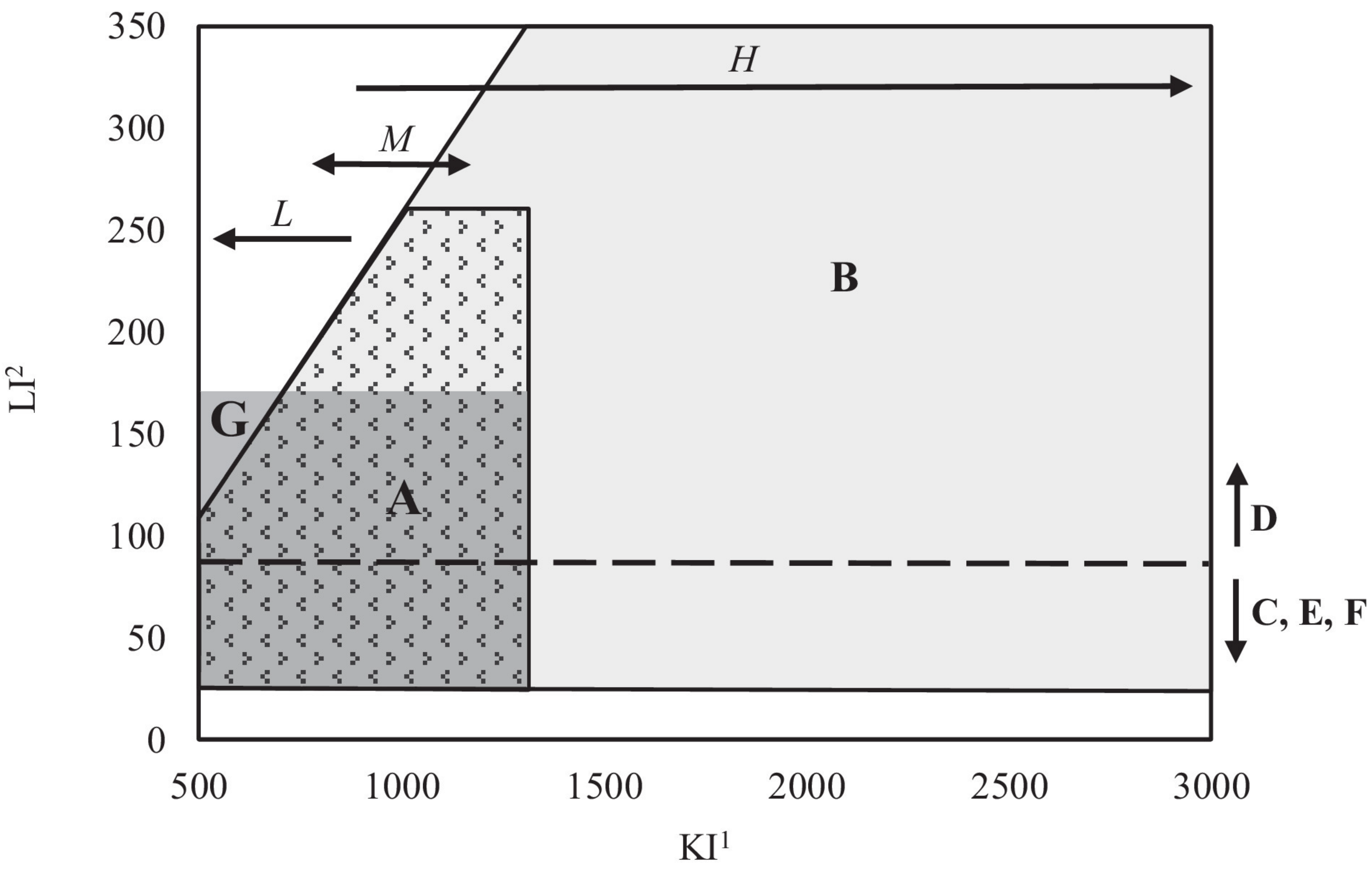
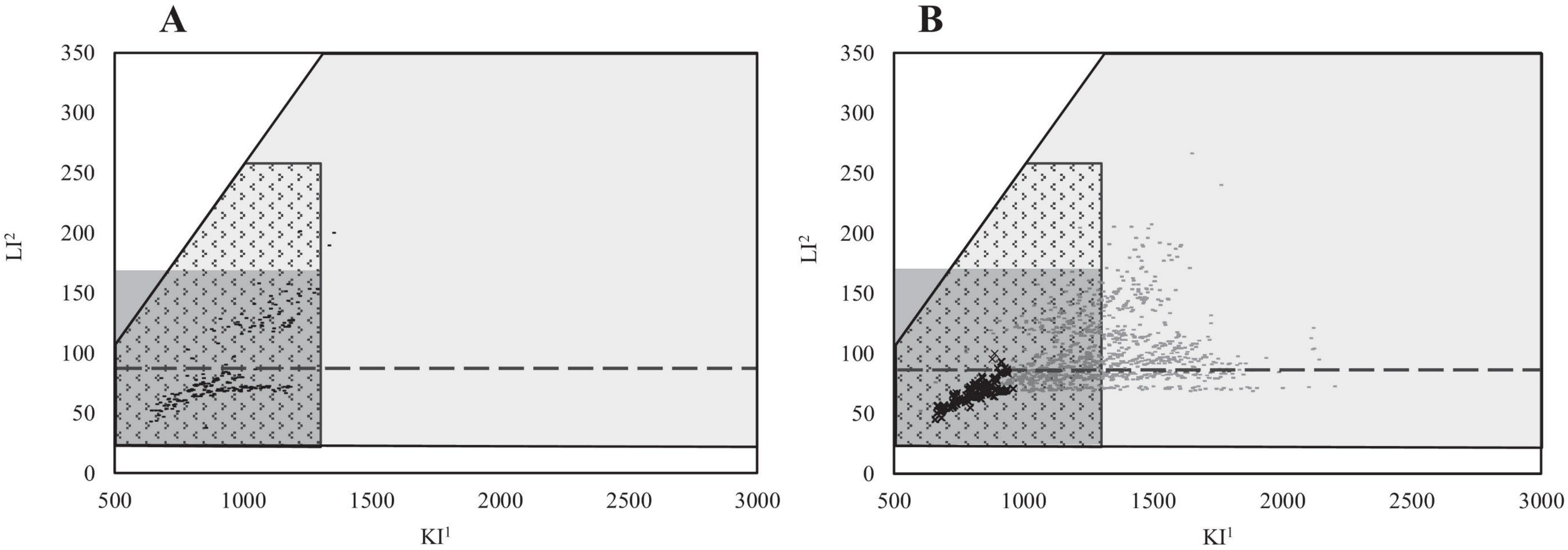


Fig. 6. KLI contour map of ASTM E1618 ILR classes with arrows for light (L), medium (M) and heavy (H) ranges (A - Gasoline, B - Petroleum Distillate, C -Isoparaffinic Products, D – Aromatic Products, E – Naphthenic – Paraffinic Products, F – Normal Alkane Products, G – Oxygenated Solvents).

ILR mapping according to ASTM E1618



KLI contour map overlay on Gasoline (A) and Petroleum Distillate (B) in light (black crosses) and heavy (grey dots) range.

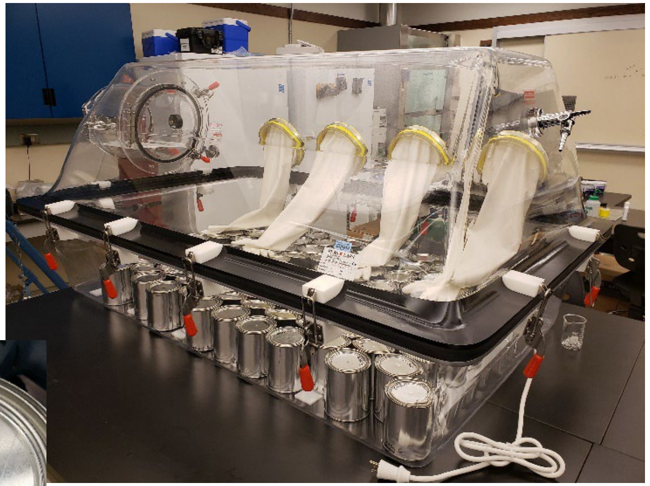
separations

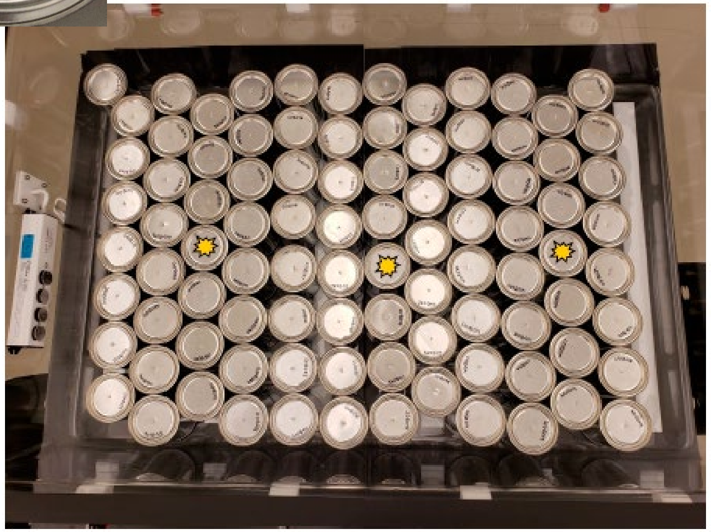
MDPI

Article

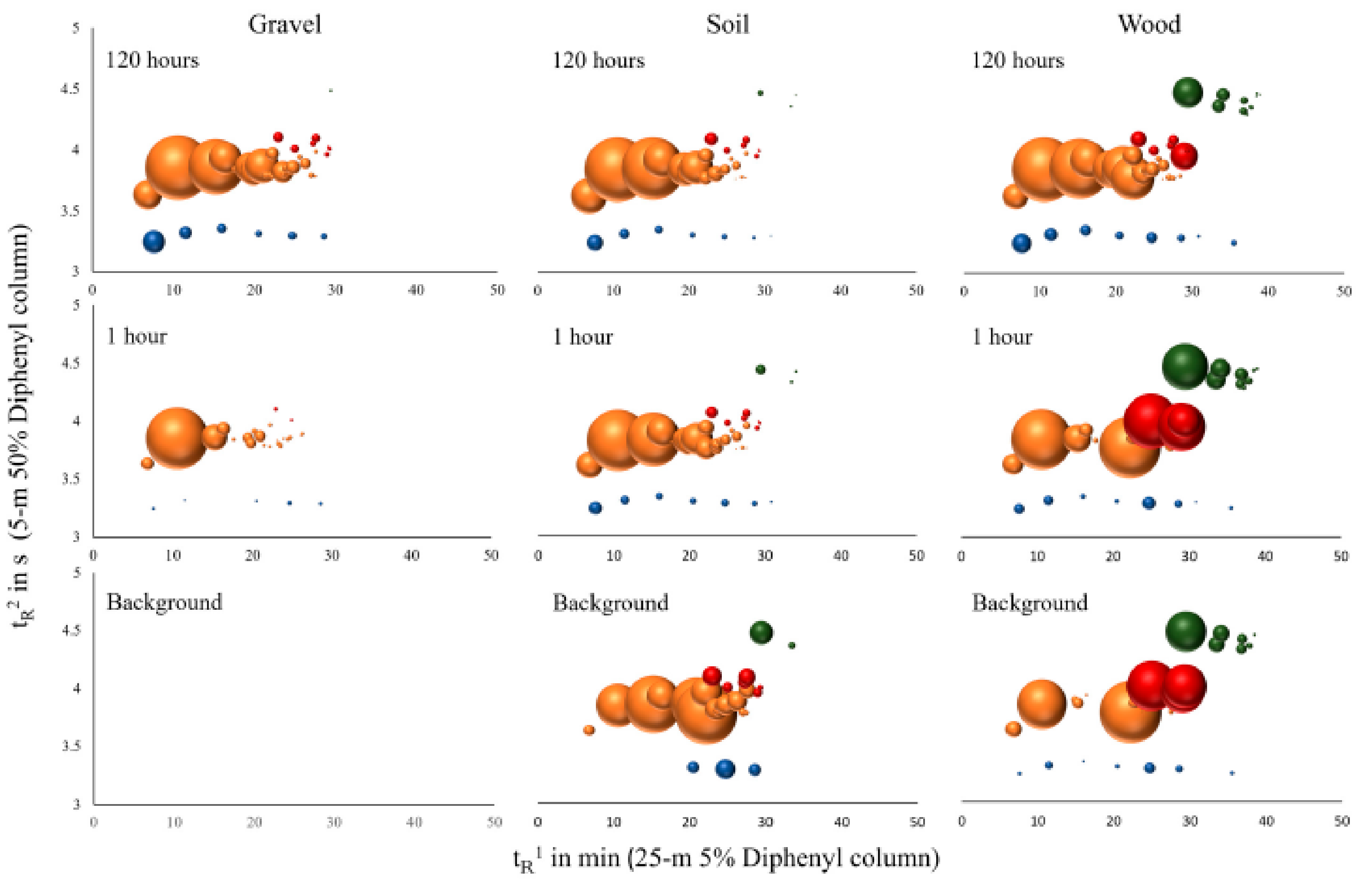
Cross-Contamination of Ignitable Liquid Residues on Wildfire Debris—Detection and Characterization in Matrices Commonly Encountered at Wildfire Scenes

Nadin Boegelsack [1,*], James Walker [2], Court D. Sandau [2,3], Jonathan M. Withey [4], Dena W. McMartin [1,5] and Gwen O'Sullivan [2]





Cross Contamination – Bubble Plots



Comparison of matrix blanks and contaminated samples after 1 h and 120 h highlighting the location of compound groups of interest

Bubble size indicating abundance of individual compounds of interest in each compound group.

Alkanes are shown in blue, alkylated aromatics in orange, indanes in red, and condensed ring aromatics in green.

Uptake Rates

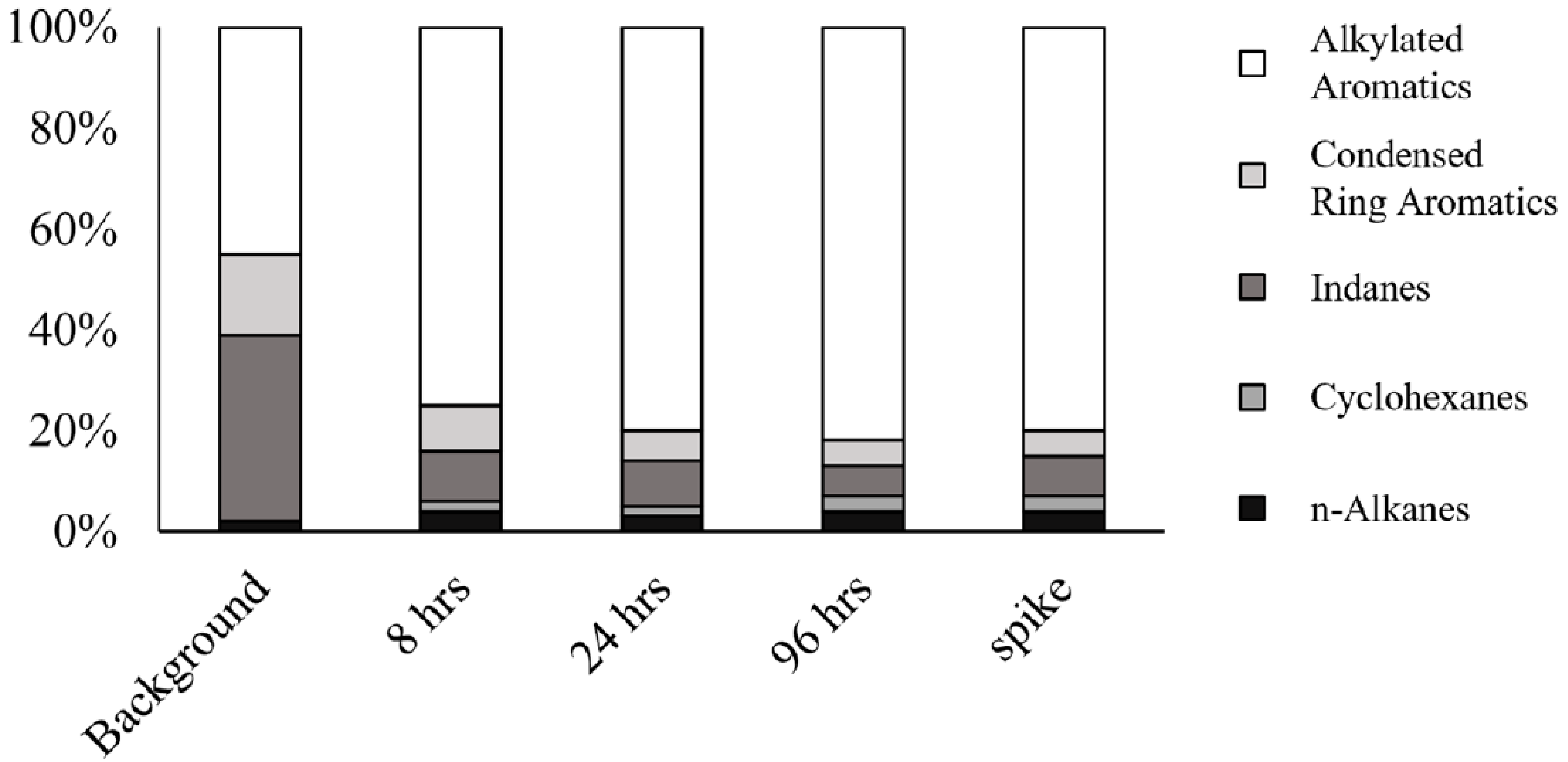
Compound	Compound Group	Henry's Law Constant (K_H) [a]	Octanol/Water Coefficient (log K_{OW}) [b]	Langmuir Isotherm Adsorption Rates		
				Gravel (r^2)	Soil (r^2)	Wood (r^2)
Heptane	n-alkanes	5.40×10^{-6}	4.66	128.6 (*0.88*)	13.3 (*0.69*)	23.8 (*0.89*)
Dodecane	n-alkanes	1.10×10^{-6}	6.1	10.5 (*0.63*)	23.3 (*0.69*)	6.4 (*0.29*)
Indane	indanes	1.20×10^{-2}	3.18	3×10^{-5} (*0.82*)	3×10^{-6} (*0.60*)	1×10^{-5} (*0.97*)
4,7-Dimethylindane	indanes	n/a	3.5	n/a	3×10^{-6} (*0.60*)	3×10^{-7} (*0.25*)
3-Ethyltoluene	alkylated aromatics	1.30×10^{-3}	3.98	5×10^{-6} (*0.97*)	7×10^{-7} (*0.74*)	3×10^{-6} (*0.94*)
4-Ethyltoluene	alkylated aromatics	1.40×10^{-3}	3.63	7×10^{-6} (*0.56*)	1×10^{-6} (*0.67*)	1×10^{-5} (*0.97*)
1,3,5-Trimethylbenzene	alkylated aromatics	1.40×10^{-3}	3.42	4×10^{-6} (*0.87*)	1×10^{-6} (*0.70*)	3×10^{-6} (*0.84*)
2-Ethyltoluene	alkylated aromatics	1.80×10^{-3}	3.53	1×10^{-5} (*0.93*)	2×10^{-6} (*0.70*)	1×10^{-5} (*0.92*)
1,2,4-Trimethylbenzene	alkylated aromatics	2.10×10^{-3}	3.63	3×10^{-6} (*0.93*)	4×10^{-7} (*0.66*)	2×10^{-6} (*0.96*)
Naphthalene	condensed ring aromatics	3.20×10^{-2}	3.3	n/a	-1×10^{-6} (*0.26*)	-7×10^{-8} (*0.51*)
2-Methylnaphthalene	condensed ring aromatics	2.80×10^{-2}	3.86	n/a	-6×10^{-7} (*0.00*)	-3×10^{-7} (*0.37*)
1-Methylnaphthalene	condensed ring aromatics	2.60×10^{-2}	3.87	n/a	-1×10^{-5} (*0.11*)	-3×10^{-7} (*0.44*)

[a] K_H in $\frac{mol}{m^3 Pa}$ determined by method Q [18]; [b] log K_{OW} taken from respective PubChem web entry for Experimental Properties > logP; Computed properties > XlogP3 value indicated in italics where no experimental value available.

Predominantly hydrophobic, with n-alkanes have the highest log K_{OW} = least polar compound group

Group type analysis

The final distributions of spiked samples are very similar regardless of the matrix, whereas the background composition varies drastically. The relative distribution pattern resembles a positive sample between 8 and 24 h of exposure.



Effects of packaging and storage on detection and characterization

Table 3 – Average target compound areas expressed as percentage of total chromatogram area for reference samples and packaging types with their respective standard deviations in brackets.
* Outlier removed

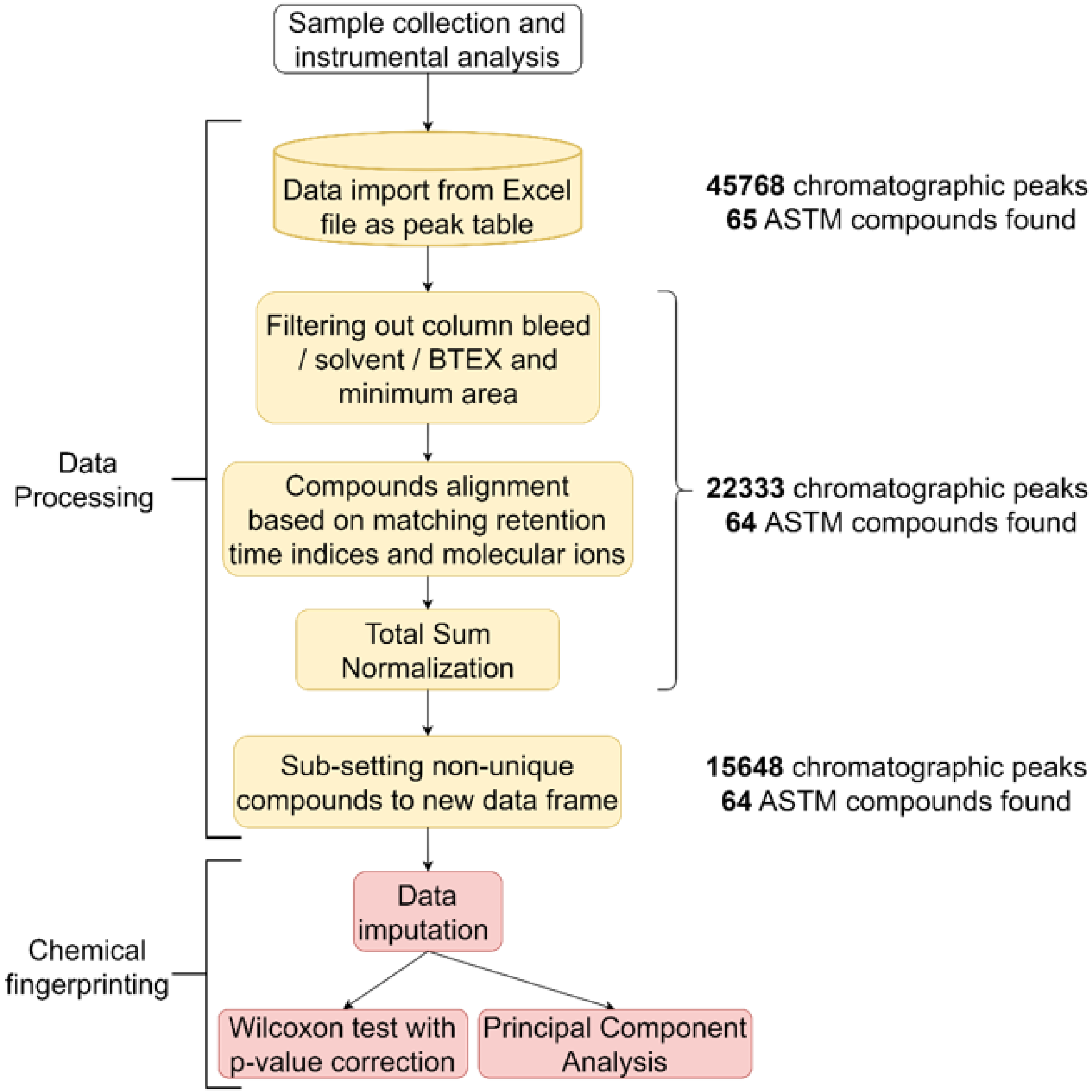
Packaging	Target Compound Area % (SD)		
	1-GB	**2-GB**	**2-FG**
Reference Background	2 (± 0.1)	-	-
Reference Contaminated (120 hrs)	7 (± 0.2)	-	-
Reference Background – Spiked	19 (± 0.3)	-	-
NBH	3 (± 0.9)	3 (± 1.4)	3* (± 0.8)
NBZ	4 (± 1.1)	5 (± 0.7)	3 (± 0.4)
RC	7 (± 0.6)	11 (± 0.9)	8 (± 0.9)
NBC	3 (± 0.2)	3 (± 0.6)	3 (± 0.3)
SB	11 (± 1.4)	14 (± 2.0)	13 (± 0.8)
DB	13 (± 0.8)	15 (± 0.8)	15 (± 1.6)
SBNB	6 (± 0.8)	9 (± 0.0)	6 (± 1.5)

Computational Fingerprints Sourcing ILRs

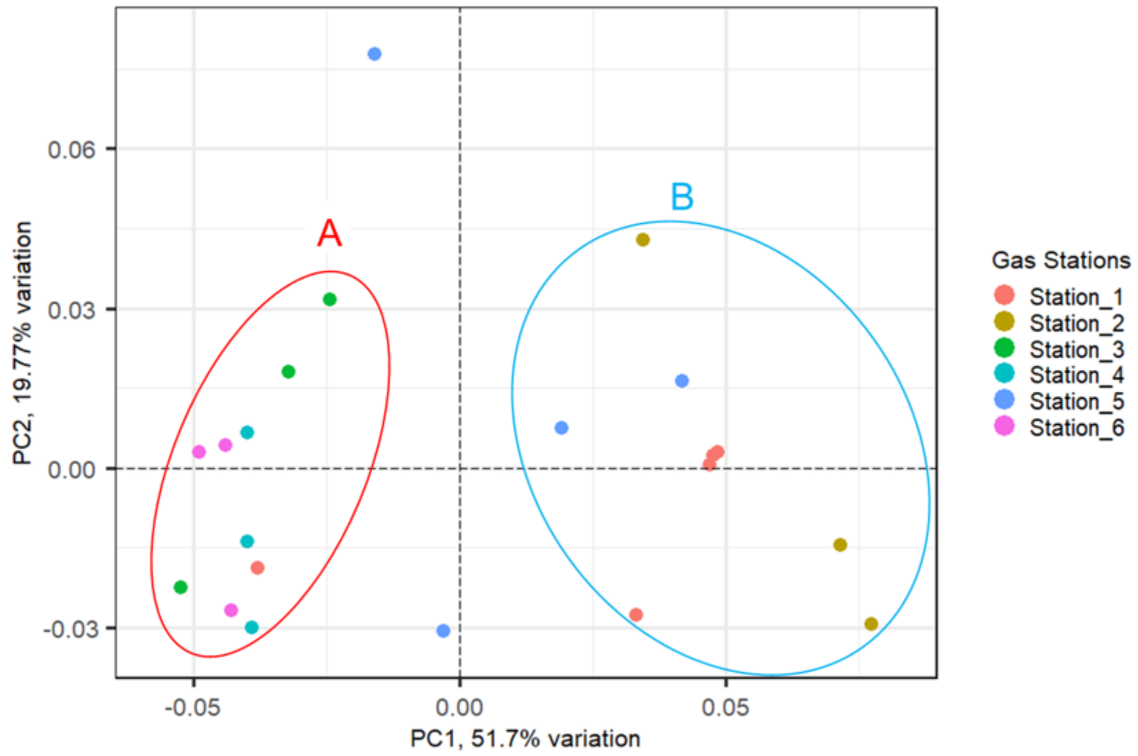
Challenges in data management of large and complex chemical data from this type of analysis can be overcome using chemometric techniques.

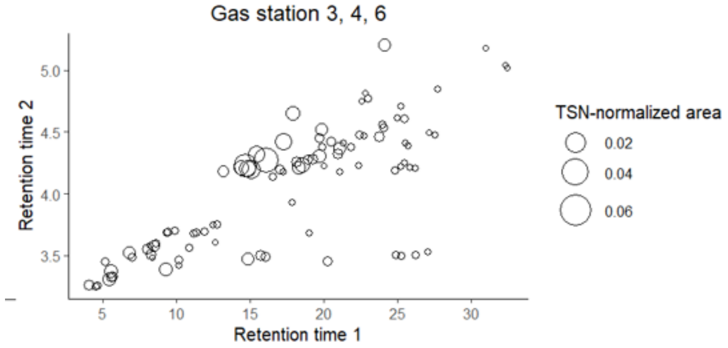
This study developed a novel chemometric workflow to identify relevant marker compounds for the distinction of ILs' types and sources for arson investigations.

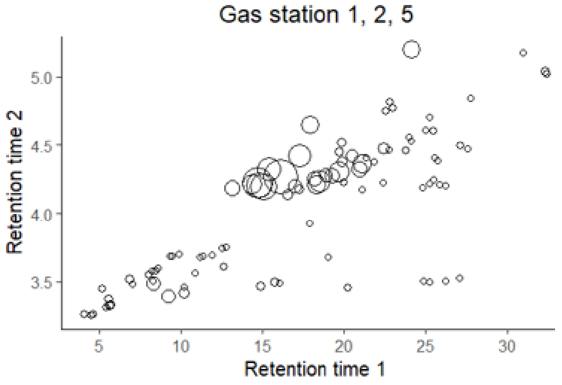
Workflow


Sample collection and instrumental analysis
Data Processing
Data import from Excel file as peak table
45768 chromatographic peaks
65 ASTM compounds found
Filtering out column bleed / solvent / BTEX and minimum area
Compounds alignment based on matching retention time indices and molecular ions
Total Sum Normalization
22333 chromatographic peaks
64 ASTM compounds found
Sub-setting non-unique compounds to new data frame
15648 chromatographic peaks
64 ASTM compounds found
Chemical fingerprinting
Data imputation
Wilcoxon test with p-value correction
Principal Component Analysis

PCA


A
B
0.06
0.03
0.00
-0.03
-0.05
0.00
0.05
PC2, 19.77% variation
PC1, 51.7% variation
Gas Stations
Station_1
Station_2
Station_3
Station_4
Station_5
Station_6


Gas station 3, 4, 6
Retention time 2
Retention time 1
TSN-normalized area
0.02
0.04
0.06


Gas station 1, 2, 5
Retention time 2
Retention time 1

On-going work

- ILR reference Library – 3 seasons, gasoline & diesels
- Non traditional ILRs
- Weathering
- Implication of extraction temperature on profile

- Screening of materials to explore background levels of ILR
- Burn studies to identify combustion compounds and presence of background ILR compounds

New Area of Research - UAV

Journal of Hazardous Materials Letters xxx (xxxx) 100013

Contents lists available at ScienceDirect

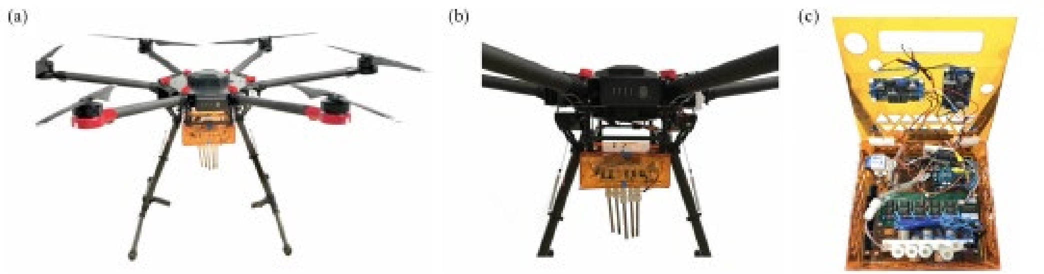
Journal of Hazardous Materials Letters

journal homepage: www.elsevier.com/locate/hazl

Frontier review on comprehensive two-dimensional gas chromatography for measuring organic aerosol

Zhaojin An[a], Xue Li[a], Zongbo Shi[b], Brent J. Williams[c], Roy M. Harrison[b,1], Jingkun Jiang[a,*]

[a] State Key Joint Laboratory of Environmental Simulation and Pollution Control, School of Environment, Tsinghua University, Beijing, 100084, China
[b] Division of Environmental Health and Risk Management, School of Geography, Earth and Environmental Sciences, University of Birmingham, Edgbaston, Birmingham, B15 2TT, United Kingdom
[c] Department of Energy, Environmental & Chemical Engineering



Atmos. Chem. Phys., 21, 5719–5737, 2021
https://doi.org/10.5194/acp-21-5719-2021

Atmospheric Chemistry and Physics
Open Access
EGU

Chemical composition of $PM_{2.5}$ in October 2017 Northern California wildfire plumes

Yutong Liang[1], Coty N. Jen[1,2], Robert J. Weber[1], Pawel K. Misztal[1,3], and Allen H. Goldstein[1,4]

[1]Department of Environmental Science, Policy, and Management, University of California, Berkeley, Berkeley, CA 94720, USA
[2]Department of Chemical Engineering, Carnegie Mellon University, Pittsburgh, PA 15213, USA
[3]Department of Civil, Architectural and Environmental Engineering, University of Texas at Austin, Austin, TX 78712, USA
[4]Department of Civil and Environmental Engineering, University of California, Berkeley, Berkeley, CA 94720, USA

Correspondence: Yutong Liang (yutong.liang@berkeley.edu)

Received: 29 August 2020 – Discussion started: 23 September 2020
Revised: 27 February 2021 – Accepted: 10 March 2021 – Published: 15 April 2021

SUMMARY – THANK YOU!

- Demand to increase the scientific rigor within Fire Investigation – natural hesitations to adopt new technologies & approaches
- GCxGC has decrease the number of false negatives in our work and has helped us get a better understanding of the implications of sample storage and preservation and weathering
- Potential for chemometric tools to provide support for fingerprinting sources